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THIRD ANNUAL REPORT- HIGH-TEMPERATURE MATERIALS AND REACTOR COMPONENT DEVELOPMENT PROGRAMS

Volume II-Materials

1 7930

February 28, 1964

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PREFACE

This report, GEMP-270B, is one of three volumes comprising the third annual report on the High-Temperature Materials and Reactor Component Development Programs (Contract No. AT(40-1)-2847) being conducted at the General Electric Nuclear Materials and Propulsion Operation for the Atomic Energy Commission.

Volumes I (GEMP-270A) and II (GEMP-270B) report the progress made from January 1, 1963 through January 31, 1964 on the unclassified and classified portions, respectively, of the materials program, and Volume III (GEMP-270C) reports the progress on that part of the contract covering instrumentation and controls. Some of these programs were terminated at the end of Fiscal Year 1963, others are continuations of Fiscal Year 1963 programs, and still others were initiated in Fiscal Year 1964. The status of each program is indicated in the more detailed breakdown of each volume given below.

This report also replaces the thirty-second bimonthly report on Ceramics and Chemistry for the period from November 15, 1963 to January 15, 1964, and the thirty-third report on Metallurgy covering the period from December 15, 1963 to February 15, 1964 except the 15 days in February. The next Ceramics and Chemistry bimonthly report, the thirty-fourth, will cover the period from February 1, 1964 to March 15, 1964. The thirty-fifth report, on Metallurgy, will cover the period from February 1, 1964 to April 15, 1964.

GEMP-270A

1. High-Temperature Reactor Materials Fabrication Research (continuation)
2. Effects of Radiation on High-Temperature Alloys (continuation)
3. Radiation Effects in BeO (continuation)
4. Fission Gas Diffusion in Unfueled Ceramic Materials (initiated FY-64)
5. Fission Product Transport Processes in Refractory-Metal Fuel Systems (initiated FY-64)
6. Internal Conversion Ceramic Fuel Element Research (initiated FY-64)

GEMP-270B

1. Fuels
 1. 1 High-Temperature Studies of Substoichiometric Urania and Urania Solid Solutions (initiated FY-64)
 1. 2 $\text{UO}_2 \cdot 9/3 \text{Y}_2\text{O}_3$ Fuel Material (terminated FY-63)
 1. 3 High-Temperature Carbides and Borides Research (initiated FY-64)
 1. 4 Coated Fuel Particle Development Evaluation (continuation)
2. Fuel Elements
 2. 1 Refractory Metal Fuel Element Materials Research (continuation)
 2. 2 Oxidation-Resistant Fuel Element Materials Research (continuation)
 2. 3 Graphite Fuel Element Materials Research (continuation)

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3. Stabilized Ceramic Fuel Elements
 - 3.1 Burnup Capabilities of Y_2O_3 -Stabilized UO_2 and Stabilized Fuel - BeO Matrix Material (initiated FY-64)
 - 3.2 Coatings For Ceramic Fuel Elements (terminated FY-63)
 - 3.3 Stabilization of UO_2 in Ceramic Fuel Elements (terminated FY-63)
 - 3.4 Fission Product Migration in Solids (terminated FY-63)
4. Other High-Temperature Nuclear Materials Research
 - 4.1 Reactor Controls, Reflectors, and Shield Materials Research (continuation)
 - 4.2 Direct Conversion High-Temperature Materials Research (continuation)
 - 4.3 High-Flux Reactor Materials Gaseous Fuels Research (initiated FY-64)

GEMP-270C

1. Circulating-Ball Reactivity Control (terminated FY-63)
2. Static Switching (terminated FY-63)
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4. High-Temperature Extension of Conventional Nuclear Sensors (continuation)
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INTRODUCTION AND SUMMARY

This report, GEMP-270B, is one of three volumes of the third annual progress report on the GE-NMPO high-temperature materials and reactor component development programs conducted during calendar year 1963 under Contract No. AT(40-1)-2847. This volume covers fourteen classified materials development programs: 1.1, studies of substoichiometric urania and urania solid solutions above 1800°C and their compatibility with refractory metals; 1.2, $\text{UO}_{2+x} \cdot 3\text{Y}_2\text{O}_3$, a composition having high-temperature stability in reducing, inert, and oxidizing atmospheres; 1.3, the physico-chemical properties of high melting borides and carbides and their stability in high-temperature gaseous environments; 1.4, coated fuel particle preparation and evaluation in BeO matrices; 2.1, refractory metal fuel element materials development for greater than 1900°C operation in non-oxidizing atmospheres; 2.2, oxidation-resistant fuel element materials for operation above 1200°C in air; 2.3, graphite fuel element materials development to improve the processing procedures, reliability, and service capabilities; 3.1, the effect of high fuel burnup on stabilized- UO_2 fuel systems and on stabilized fuel - BeO-matrix fuel elements; 3.2, coatings for ceramic fuel elements to inhibit fission product release; 3.3, stabilization of UO_2 in ceramic fuel elements to extend high-temperature limits; 3.4, fission product migration in ceramic systems; 4.1, development of new or improved reactor control, reflector, and shield materials; 4.2, direct conversion high-temperature materials for use in high-temperature reactors; and 4.3, high-flux reactor gaseous fuel materials research.

Significant results achieved in these programs are as follows:

Studies of urania vaporization in flowing dry hydrogen showed that limiting oxygen-to-uranium ratios of about 1.90, 1.88, and 1.87 are achieved at temperatures of 2200°, 2400°, and 2600°C, respectively, but that these values are sensitive to moisture content (oxygen partial pressure). Samples of UO_2 plus uranium metal homogenize rapidly at temperatures above 2000°C, facilitating the fabrication of substoichiometric urania specimens for vaporization and compatibility studies. Sintered $\text{UO}_{2.00}$ specimens encapsulated in tungsten and rhenium were stable after testing in hydrogen at 2400°C for 8 hours, whereas $\text{UO}_{2.00}$ similarly tested in a tantalum capsule lost nearly 1 percent in weight and had a final oxygen-to-uranium ratio of 1.86.

Using Y_2O_3 additive to produce an oxygen-deficient lattice in UO_2 , it was shown that: (1) the oxidation rate becomes more rapid as the oxygen-to-metal ratio is reduced; (2) the onset of parabolic oxidation occurs at lower temperatures for an oxygen-deficient lattice than for nearly stoichiometric UO_2 ; and (3) the oxygen self-diffusion coefficient is about the same in $\text{UO}_{2.67} - 40\text{Y}_2\text{O}_3$ (mole %) as in UO_2 .

The $\text{UO}_{2+x} \cdot 3\text{Y}_2\text{O}_3$ fuel composition shows promise for application in reactor systems operating for several thousand hours at temperatures up to 1700°C in both oxidizing and reducing atmospheres. This fuel can be cycled between oxidizing and reducing atmospheres without significant changes in strength or physical integrity.

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Processes were developed for: (1) the rapid comminution of friable fuel compacts to powder in the 37- to 53-micron size range (40-percent yield); (2) spheroidizing fuel particles at rates of approximately 400 grams per hour in a direct-current plasma flame (90-percent yield); (3) depositing dense BeO or Y₂O₃-stabilized ZrO₂ coatings on fuel spheres; and (4) uniformly dispersing coated and uncoated fuel spheres in an extruded and sintered BeO matrix.

The composition W - 48UO₂ - 12ThO₂ (vol %) clad with W - 25Re showed no detrimental effects after heating for 10 hours at 2800°C and 1 hour at 2900°C in hydrogen. Adding thorium to uranium increases the melting point and reduces the fuel loss at 2400°C by a factor of 2.5. Tantalum-clad W-UO₂-ThO₂ specimens remained leak-free for at least 365 hours and as long as 1278 hours at 2200°C. Leaks in Ta-clad W-UO₂ specimens appeared to be caused by free uranium metal which permeated the grain boundaries of the cladding in a few hours at 2200°C if the oxygen-to-uranium ratio of the fuel was less than 2.0. An in-pile test of Ta-clad W-UO₂ was operated for 175 hours at 1915°C and 2 hours at 2200°C with no abnormal activity detected and no appreciable core - cladding reactivity noted.

Brazing systems for refractory metals for a range of brazing temperatures from 1900°C to 2800°C were developed.

Uranium dioxide, contained in a matrix of either chromium or iron and clad with Fe-Cr-Al-Y alloy, remained stable for at least 1200 hours at 1250°C in flowing air.

A chromium content of 15 weight percent in Fe-Cr-Al-Y provided oxidation resistance equivalent to the 25-weight percent chromium alloy; this alloy was also less susceptible to embrittlement. However, the addition of 1 weight percent yttrium was found to be essential to stabilize the protective alumina film which provides the long-time oxidation resistance. Fe-Cr-Al-Y alloy and Nb-modified 80Ni - 20Cr alloy were found to be highly corrosion resistant in low-pressure steam at 730°C for at least 2000 hours. At high temperatures (1150°C to 1260°C), the Fe-Cr-Al-Y alloy showed resistance to steam corrosion comparable to its oxidation resistance in air.

Both ruthenium and cobalt improved the ductility of chromium in much the same manner as rhenium additions.

Fuel elements, composed of BeO containing 20 weight percent UO₂ as the gadolinia-modified F-204 composition, retained 70 percent of their strength and showed less than 1-percent change in dimensions after irradiation to 3.15×10^{20} fissions/cm³ at 1175°C to 1370°C. The creep rates of BeO fueled with the F-204 composition, with UO₂ contents from 2 to 20 weight percent, were shown to be linear with the parameter, stress/(grain size)², for grain sizes up to 50 microns.

Comparison of I¹³¹ release kinetics of 6BF-116 and 6BF-204 showed little difference in release kinetics below the BeO-Y₂O₃ eutectic temperature (1580°C); above this temperature, the liquid phase (which forms in 6BF-116 but not in 6BF-204) results in a very significant increase in release rate from the 6BF-116.

The release of I¹³¹, Kr⁸⁵, and Xe¹³³ from BeO-dispersed oxide fuel elements containing 6 to 8 weight percent fuel was found to be diffusion-controlled, and has an apparent activation energy of approximately 135 kcal/mole. The release of Xe¹³³ from powder samples of the fuel phase which is dispersed in 6BF-116 is also diffusion-controlled and has an activation energy of about 85 kcal/mole. Fission product release from dynamic in-pile tests on fuel elements indicated that BeO bodies containing noncontinuous dispersions of fuel are promising materials for retaining fission products at high temperatures.

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Hydriding technology was extended to include an automated cycle which significantly reduces labor costs and provides certain improvements in physical properties in a range of specimen sizes. The long-time nuclear and thermal stability of clad YH_x was demonstrated for 11,000 hours in air at 940° to 1050°C and in a reactor test at 880° to 940°C in air for 5000 hours. Titanium hydride was found to be capable of self-supported, unclad operation in air at temperatures up to 540°C . Through the use of appropriate additives, e. g., TiC , TiB_2 , B_4C , WB_2 , etc., it was shown that performance can be tailored for maximum efficiency for shielding applications.

Control rod materials such as the rare earth oxides of Eu, Gd, and Dy, clad in Mo or Mo - 50Re, showed generally good thermal and dimensional stability after 2000 hours at 1650°C in dry hydrogen.

$12\text{Y}_2\text{O}_3$ - 80ZrO_2 - 8Zr was found to have good thermoelectric power generation properties, having a maximum dimensionless figure of merit of 0.8 at 2200°C . A single cell device produced approximately 1.5 watts of power at 30 amperes.

1. FUELS

1.1 HIGH-TEMPERATURE STUDIES OF SUBSTOICHIOMETRIC URANIA AND URANIA SOLID SOLUTIONS (57071)

The objective of this study is to determine the physico-chemical relationships involved in the use of substoichiometric urania and urania solid solutions at temperatures above 1800°C, and to define the reactions, if any, and the kinetics of these reactions with various refractory metals and alloys.

The scope of this study consists of:

1. Physical chemistry of UO_2 and UO_2 solid solutions.
 - a. Effect of temperature and oxygen partial pressure on the congruent vaporization composition.
 - b. Effect of substoichiometry on the melting point.
 - c. Solubility of metallic uranium in UO_2 .
 - d. Solubility of oxygen in liquid uranium.
 - e. Phase studies and kinetics of reactions in the $\text{UO}_2\text{-Y}_2\text{O}_3$ and $\text{UO}_2\text{-ThO}_2$ systems.
2. Compatibility of UO_2 and UO_2 solid solutions with refractory metals and alloys.
 - a. Kinetics of reactions.
 - b. Products of reactions.
 - c. Resultant stoichiometry.
 - d. Effect of thermal cycling.

PHYSICAL CHEMISTRY

Congruent Vaporization of UO_2

A number of investigators have identified the presence of metallic uranium in otherwise pure UO_2 after heating at temperatures above 1800°C in vacuum, hydrogen, or an inert atmosphere.*†‡ It was shown in an earlier report§ that, by heating UO_2 pellets in a flowing dry hydrogen atmosphere at 2400°C, a composite composition with an oxygen-to-uranium ratio as low as 1.88 can be achieved. These pellets contained a uranium metal phase as indicated by their tendency to absorb hydrogen and disintegrate at low temperatures, by microprobe examination of the metal phase, and by X-ray diffraction examination. The UO_2 pellets approached this limiting composition asymptotically with increasing weight loss of the specimen. These studies were continued to further determine the chemical behavior of UO_2 while vaporizing in various gaseous environments.

*J. S. Anderson, et al., "Decomposition of Uranium Dioxide at its Melting Point," *Nature*, Vol. 185, 1960, p. 915.

†R. Columbo and G. Frigerio, "On the Occurrence of Uranium Metal Particles in Fused UO_2 ," *Journal of Nuclear Materials*, Vol. 5, No. 2, 1962, pp. 259-261.

‡R. G. Robins, "The Precipitation of Uranium Metal in Uranium Dioxide Single Crystals," *Journal of Nuclear Materials*, Vol. 7, No. 2, 1962, pp. 218-219.

§"Second Annual Report - High-Temperature Materials and Reactor Component Development Programs; Volume II - Materials," GE-NMFO, GEMP-177D, February 28, 1963, pp. 27-39.

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New vaporization studies were carried out at GE-NMPO in a furnace in which the oxide insulation was replaced by tungsten and molybdenum radiation shields. The tungsten heating element and other furnace details were reported previously.* With only metallic hardware in the furnace, the internal sources of water vapor from hydrogen reduction of refractory oxides have been minimized. The dewpoint of the hydrogen environment in the furnace is closely monitored at the entrance and exit lines and sometimes through a special probe located in the hot zone of the furnace.

The hydrogen flow is directed downward through a 2.5-centimeter diameter muffle in which a test specimen is suspended in a rhenium wire basket. The uranium oxide vapor exits from the muffle and deposits almost exclusively on a molybdenum shield located just below the muffle exit. The rhenium basket has been used for numerous runs with no evidence of deterioration or attack by the UO_2 pellets. The pellets weighed nominally 10 grams and were 1.0 centimeter in diameter by 1.3 centimeters long. They were prepared by cold pressing and sintering for 2 hours in hydrogen at 1700°C to between 97 and 98 percent of theoretical density. The average oxygen-to-uranium ratio of the sintered pellets ranged from 2.003 to 2.008 as determined by ignition (at 1000°C) of the entire pellet in air to U_3O_8 . The pellets consisted of a single-phase UO_2 fluorite-type structure.

During vaporization, the pellets decreased in size uniformly along all surfaces, indicating that the hydrogen flow was smooth and the temperature of the specimen was uniform. The loss rate of the pellets varied with hydrogen flow rate and with temperature in a regular manner. Upon cooling after vaporization, the hydrogen gas was replaced by argon at about 1000°C to prevent disintegration because of hydrogen absorption by the uranium metal. Disintegration was observed to occur even at room temperature in the presence of hydrogen. After vaporization, some pellets showed evidence of UN phase in the metal located near the surface. The nitrogen impurities in the argon or hydrogen were believed to be responsible for this contamination. The amount of UN phase present has a negligible effect on the oxygen-to-uranium ratio.

Vaporization of $\text{UO}_{2.006}$ in Dry Hydrogen - Vaporization tests were performed at 2200° , 2400° , and 2600°C for various times. These tests led to limiting oxygen-to-uranium ratios of approximately 1.90, 1.88, and 1.87 at 2200° , 2400° , and 2600°C , respectively. Whether these ratios may be interpreted as indicating solely the effect of temperature is doubtful, since there were some variations in the moisture content of the hydrogen. Furthermore, for a given moisture content, the corresponding oxygen partial pressure increases rapidly with temperature, as discussed later in this report. Typical results are given in Table 1.1-1. Additional results were reported previously.†

Vaporization of UO_2 Containing Added Uranium - A description of the above limiting oxygen-to-uranium ratios as congruent vaporization compositions would be more convincing if the same values could be achieved when starting with samples in which the oxygen-to-uranium ratio was less than the limiting value. This was done, using the following method of sample preparation.

A 3-millimeter hole is made in the center of one end of a pellet extending about half-way down the axis. This provides a black body hole for temperature measurements and also provides a place to insert uranium metal to make a composite specimen. Several composite specimens (calculated to be $\text{UO}_{1.82}$) were heated for various times at temperatures from 1800° to 2600°C in dry hydrogen. In all cases, the metal insert grew and appeared as a protuberance after the test. At the lower temperatures, this growth was a voluminous,

* J. B. Conway, D. G. Salyards, W. L. McCullough, and P. N. Flagella, "Stress Rupture and Creep Properties of Refractory Metals," GE-NMPO, TM-63-4-12, April 1963.

† "High-Temperature Materials Program Progress Report No. 30, Part B," GE-NMPO, GEMP-30B, December 31, 1963, p. 36.

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TABLE 1.1-1
VOLATILITY AND COMPOSITIONAL CHANGES OF URANIA
PELLETS HEATED IN DRY HYDROGEN

Temperature, °C	Time, hr	Exit Moisture ^a Content, mm Hg	Sample Density, g/cm ³		Weight Loss, %	Oxygen-To- Uranium Ratio	
			Before ^b	After		Initial ^c	Final
1700	3	0.11	10.687	10.930	0.03	2.006	1.994
2200	2		10.679	10.786	3.06	1.823	1.852
	4		10.711	10.796	4.05	1.880	1.889
	6	0.08	10.715	10.849	5.37	1.890	1.898
	4		10.572	10.785	2.00	1.900	1.911
	6		10.703	10.846	6.47	1.900	1.901
	2		10.655	10.824	1.80	2.006	1.974
2400	1	0.16	10.702	10.832	6.85	1.822	1.843
	3	0.20	10.696	10.824	19.62	1.817	1.860
	4	0.12	10.690	10.829	29.19	1.823	1.869
	2	0.11	10.702	10.791	15.73	1.816	1.863
	6	0.12	10.663	10.860	34.35	1.822	1.877
	1		10.721	10.785	7.73	1.823	1.843
	4	0.14	10.637	10.711	24.85	1.870	1.886
	2	0.12	10.693	10.757	12.43	1.871	1.875
	4		10.676	10.833	19.96	1.870	1.873
	4	0.09	10.708	10.856	23.70	1.880	1.876
	2	0.16	10.711	10.838	15.00	1.880	1.881
	1		10.690	10.794	5.53	1.880	1.881
	4	0.13	10.703	10.743	18.75	1.890	1.880
	2	0.11	10.707	10.777	13.57	1.890	1.885
	1.5		10.729	10.902	10.08	2.006	1.916
2600	<0.1	0.23	10.667	10.808	3.22	1.808	1.836
	0.25	0.11	10.663	10.839	8.99	1.804	1.820
	0.5	0.24	10.689	10.838	22.68	1.817	1.839
	0.75	0.30	10.681	10.850	29.30	1.825	1.854
	1.0	0.24	10.691	10.838	50.27	1.810	1.879
	0.5	0.13	10.704	10.872	15.27	1.860	1.871
	1.0	-	10.713	10.589	29.94	1.861	1.862
	0.5	0.16	10.671	10.908	14.84	1.870	1.886
	1.0	0.17	10.689	10.850	29.06	1.871	1.872
	0.5	0.17	10.727	10.860	15.09	1.870	1.889
	1.0		10.716	10.840	23.18	1.880	1.873
	0.5	0.19	10.700	10.822	17.81	1.890	1.877
	1.0	0.30	10.706	10.838	31.08	1.890	1.872
	2.0	0.12	10.672	10.937	64.76	2.006	1.894
	1.5	0.14		10.834	55.02	2.006	1.873

^aMoisture contents of the inlet hydrogen were invariably in the range of 0.01 to 0.03 mm of Hg as measured by a Beckman hygrometer.

^bDensity of the UO₂ pellet before adding uranium.

^cCalculated for the composite samples on the basis of 2.006 for the UO₂ pellet and neglecting oxygen impurity in the added metal.

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porous mass; at higher temperatures, it was a dense, pointed spire. Subsequent examination showed this growth to be urania, indicating that at these temperatures oxygen diffuses into the molten metal from the surrounding oxide much faster than the metal seeps into the oxide. This was expected on the basis of diffusion coefficients extrapolated from data given by Belle.*

Microscopic examination of these composite samples showed the following.

1. The uranium metal insert was converted to predominantly urania in 3 hours at 1800°C and 1 hour at 2000°C. The distribution of uranium metal was slightly inhomogeneous: there was more uranium metal in the original uranium insert area than in the original UO₂ area. Treatments of 1 hour at 2400°C and 5 minutes at 2600°C resulted in a uniform distribution of uranium metal. In all cases, there was uniform distribution of fine uranium particles with agglomerations of uranium metal at the surface, pores, and grain boundaries.
2. At the higher temperatures (>2400°C), there was another phase present in the large uranium particles. The second phase was predominantly concentrated in the surface particles; X-ray diffraction studies showed it to be predominantly UN. Only a trace amount of this phase was found in the interior of the samples. The formation of the nitride is believed to be caused by nitrogen impurity in the argon which was used as the cooling atmosphere from about 1000°C.

On the basis of these observations, it is reasonable to consider the composite samples as the equivalent of uniform substoichiometric UO₂ for purposes of volatility tests, since the time required to achieve uniformity is small relative to the duration of tests at each temperature.

As a preliminary series, composite samples were made with an approximate composition of UO_{1.82} and were subjected to heat treatments of various durations at temperatures of 2200°, 2400°, and 2600°C in dry hydrogen. In all cases, the oxygen-to-uranium ratio increased, the extent depending upon the amount of weight loss. Additional composite samples were prepared with calculated oxygen-to-uranium ratios of 1.86, 1.87, 1.88, 1.89, and 1.90. The results of these tests on composite samples and several other tests on as-sintered UO₂ specimens are summarized in Table 1.1-1. These data are plotted, together with previously reported data† on as-sintered UO₂ specimens, in Figures 1.1-1, 1.1-2, and 1.1-3. Included are a number of results obtained using induction heating. Table 1.1-1 includes sample density and hydrogen moisture contents before and after testing. A discussion of the latter appears later in this report. The increase in density is largely the result of additional sintering rather than compositional changes as suggested by results of the single test at 1700°C. The oxygen-to-uranium ratio dropped slightly in this test which is not unexpected since the moisture content (i. e., oxygen partial pressure) was appreciably less in the tungsten furnace used, than in the refractory-oxide-lined furnace used for the previous sintering.

The results demonstrate that the same composition is approached from either side of the binary system and that this composition represents a congruency point at the temperature and oxygen pressures achieved in these experiments. The ease of preparing composite samples makes it possible to define this limiting composition with a minimum number of vaporization tests.

* J. Belle, Editor, *Uranium Dioxide, Properties and Nuclear Applications*, Superintendent of Documents, U. S. Government Printing Office, pp. 308, 318.

† "High-Temperature Materials Program Progress Report No. 30, Part B," GE-NMPO, GEMP-30B, December 31, 1963, pp. 35-38.

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Fig. 1.1-1—Weight loss of urania versus final oxygen-to-uranium ratios in hydrogen at 2200°C

Fig. 1.1-2—Weight loss of urania versus final oxygen-to-uranium ratios in hydrogen at 2400°C

Effect of Water Vapor Content - Vaporization of urania produces several vapor species; the relative amounts varying if the atmosphere is one in which the composition of the solid phase can vary. Such is the case, for example, in the high-temperature evaporation of $\text{UO}_{2.006}$ in dry hydrogen. The solid composition varies with time, as does the gross composition of the vapor phase, until the congruent point is reached. For a complete description of the vapor phase, the existence of a finite oxygen partial pressure must be recognized, the magnitude of which will determine the position of equilibrium in the vapor between the various species such as UO and UO_2 and, consequently, the composition of the solid phase as well.

Therefore, it is necessary to measure the oxygen partial pressure as part of the definition of a congruent vaporization composition. For a gaseous environment containing hydrogen, essentially all oxygen may be assumed to be present as water vapor; thus,

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Fig. 1.1-3—Weight loss of urania versus final oxygen-to-uranium ratios in hydrogen at 2600°C

dewpoint measurements can be used as an analytical method to indicate oxygen partial pressures. Measuring the oxygen partial pressure in this manner has several limitations; these are:

1. Oxygen and hydrogen must be assumed to equilibrate quickly with respect to moisture formation. This is a reasonable assumption at the temperatures of interest ($>1800^{\circ}\text{C}$).
2. The hydrogen must be sampled at the point of interest, i. e., at the location of the urania pellet, to avoid altering the dewpoint by diluting with other furnace purge gases and by gettering of moisture by colder downstream furnace components.
3. Urania vapors of changing stoichiometry are condensing out in the probe tube which may influence the observed dewpoint by a secondary reaction with the hydrogen.

In the earlier tests, the dewpoints measured at the exit end of the furnace were thought to be of significance in interpreting results of volatility tests. However, item 2 above indicates that this type of data may not be a reliable or sensitive measure of the situation that actually exists at the site of the sample. To rectify and clarify this situation, a 0.32-centimeter molybdenum tube was inserted from the top of the vertical muffle to permit sampling the gas immediately upstream of the urania pellet. At the temperatures of interest and the moderate hydrogen flow rate of about 4 liters per minute through the 2.5-centimeter diameter muffle, the location of this sampling probe is assumed to be representative of the atmosphere surrounding the specimen.

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In the earlier samplings with this probe device, an Alnor (manual) Dewpointer was used. This instrument also was used for the measurements shown in Table 1.1-1 and all previous reports. Continuous readings are now being obtained with Beckman hygrometers installed on both the exit line and hot zone probe. The Beckman instruments invariably indicate less moisture than the Alnor Dewpointer, a discrepancy which has not been resolved. However, relative values are believed to be reliable and the ability to record moisture contents continuously has revealed useful information.

To operate the Beckman instruments at a stable flow rate, the effluent gas flow was constricted to build up a pressure of 2.5 psig within the furnace. This was the only variation of previous operating procedure except that the hot zone probe (pulling gas upwards) disturbed the regular downward flow of the gas through the hot zone. The amount of gas removed by the probe was about one-fourth or less of the total volume of gas flowing through the muffle.

Several empty furnace runs to 2400°C using this sampling device showed that the moisture contents of the hot zone and exit hydrogen were approximately the same, ranging from about 50 to 100 ppm. This level of moisture was somewhat higher than in the inlet hydrogen, the difference presumably representing oxygen impurity in the hydrogen.

With a UO_2 sample in the hot zone, a rapid increase of moisture was observed at that location when the temperature reached 2400°C, but this moisture increase was essentially undetected at the furnace exit. The amount of this moisture decreased with time at temperature, eventually leveling off to a constant value. To determine if the increase in moisture was due to water associated with the test specimen, a similar test was run in a helium atmosphere; no moisture increase was observed.

Thus, the moisture increase undoubtedly results from hydrogen reacting with the urania vapor or with the solid phase, and the decrease with time as UO_2 volatilization proceeds results from a decreasing oxygen-to-uranium ratio in the residual pellet and, hence, a decreasing activity of oxygen in the vapor phase. Based on this reasoning, specimens of various initial oxygen-to-uranium ratios should show different moisture content versus time profiles at temperature. To test this hypothesis, three tests each were run at 2200°C and at 2400°C with specimens of 2.006, 1.880, and 1.823 initial oxygen-to-uranium ratios. The last two compositions were prepared by the composite sample method previously described. Continuous moisture contents of the hydrogen were monitored at both the hot zone and exit. The results, Figures 1.1-4 and 1.1-5, show that the magnitude and duration of the increased moisture contents depend upon the initial urania composition. That a moisture increase occurs at all for a starting composition of 1.823 is probably due to the fact that the pellet (initially 2.006 oxygen-to-uranium ratio) and added uranium metal have not reached equilibrium during the first moments at temperature. The rate of equilibration increases with temperature as indicated by the data in Figures 1.1-4 and 1.1-5 which show that the rate of decrease of the increased moisture with decreasing oxygen-to-uranium ratio is greater at the higher temperature.

It is also clear that the moisture content of the hydrogen measured at the exit does not adequately reflect the moisture content at the site of the sample. This was shown in another vaporization experiment reported previously* with a pellet of UO_2 .006 heated at 2400°C to a weight loss of nearly 36 percent in moist hydrogen. The final oxygen-to-uranium ratio was found to be 2.010 which is significantly different from that obtained in dry hydrogen. The moisture content measured at the exit was 0.50 mm of Hg (about 600 ppm). The true moisture content in the hot zone was undoubtedly higher inasmuch as a small leak of furnace cooling water upstream from this point was discovered after this test. Consequently,

*Ibid., p. 36,

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Fig. 1.1-4 - Hot zone moisture contents versus time at 2200°C

the exit moisture contents shown in Table 1.1-1 may not properly reflect variations in hot zone moisture contents. This may explain the occasional scatter in results from different experiments. However, the general importance of moisture (oxygen partial pressure) in controlling the attainable urania stoichiometry was demonstrated. The oxygen partial pressure at the specimen site must now be defined.

For conversion of moisture contents in hydrogen to equivalent oxygen partial pressures, the following equation for the free energy of formation for water was used:

$$\Delta F^{\circ} = -58,900 + 13.1T(^{\circ}\text{K})$$

where

$$\log P_{\text{O}_2} = \frac{2\Delta F^{\circ}}{2.303RT} + 2 \log \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}}$$

Representative calculations for a nominal hydrogen pressure of 800 mm of Hg were made by Atlas and Moser.* These have been extended to other temperatures and moisture contents as shown in Figure 1.1-6. Two important observations from these calculations are (1) the extremely small degree of dissociation of water even at 2600°C and (2) the significant sensitivity of oxygen partial pressure to temperature for a given moisture content.

* L. M. Atlas and J. B. Moser, "Tables of Oxygen Pressures Calculated from the Hydrogen-Water System and from the Dissociation of Cupric Oxide," Argonne National Lab., Report ANL-6747, July 1963.

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Fig. 1.1-5—Hot zone moisture contents versus time at 2400°C

The latter point is particularly important with respect to the effect of temperature on the congruent vaporization composition. Within the limits of the data shown in Figures 1.1-1 through 1.1-3, there is very little difference in the temperature range from 2200° to 2600°C. However, as shown in Figure 1.1-6, it is clear that for a given moisture content, the oxygen partial pressure varies by a factor of about 30 over this same temperature range. A proper comparison of temperatures must be made at a single oxygen partial pressure.

Thermodynamic Considerations of the Congruent Vapor Composition

The principal vapor species present over the UO_{2+x} system were identified by Chupka* to be UO_3 , UO_2 , and UO . DeMaria, et al.,† made a mass spectrometric study of the uranium - oxygen system and determined the free energies of the reaction between the gaseous species. The vaporization of UO_2 in the experiments reported here were carried out in the hydrogen - water system and, assuming that equilibrium was attained, the free

* W. A. Chupka, ANL 5753 (1957), p. 65; ANL 5786 (1957), p. 73.

† G. DeMaria, R. P. Burns, J. Drowart, and M. G. Inghram, "Mass Spectrometric Study of Gaseous Molybdenum, Tungsten, and Uranium Oxides," *Journal of Chemical Physics*, Vol. 32, 1960, p. 1373.

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Fig. 1.1-6—Oxygen partial pressure in hydrogen (800 mm total pressure) at various temperatures and moisture contents

energy of the hydrogen - oxygen - water reaction could be used with the results of DeMaria, et al., to determine the vapor species present in the system. The predominant vapor species at the congruent vapor composition were calculated to be UO_2 , UO , H_2O , and H_2 . All other species (i. e., UO_3 , O_2) are several orders of magnitude lower in pressure, although monoatomic uranium may be present to the extent of a few percent. The furnace elements such as Re, W, and Mo were assumed to have a negligible effect on the vaporization of the UO_2 . Initially, UO_3 vapor may be present since the $\text{UO}_{2.00}$ pellets must have a vapor composition with oxygen-to-uranium ratios greater than 2.00, but it cannot be present at the congruency point.

The oxygen and uranium that leave the solid at the congruency point are distributed among the three principal vapor species H_2O , UO , and UO_2 to give a net oxygen-to-uranium ratio of 1.88. Since there is also a net flow of water into the system from the outside, the total water pressure would be the sum of these two sources. The amount of water formed during vaporization of the solid may be small enough that no net increase in the water content occurs. The vapor pressure of one of the uranium vapor species must

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be determined before further calculations of the relative distribution of oxygen and uranium among the vapor species can be made.

Since the congruency composition was approached from both sides of the binary UO_2 -U system, the effect of impurities causing a reduction of the UO_2 to this composition was ruled out. Low oxygen-to-uranium ratios were obtained by vaporization of UO_2 pellets in atmospheres other than hydrogen. Thus, it can be assumed that hydrogen is not a necessary factor other than to control the oxygen partial pressure. The presence of hydrogen, however, may give rise to a possible gaseous uranium hydroxide species that would enable a lower oxygen-to-uranium ratio to be achieved than might be obtained in other gaseous environments. At present, the importance of this factor has not been determined.

If the $\text{UO}_{1.88}$ composition were two phase, i. e., a liquid uranium phase and a solid UO_{2-x} phase, then the vapor composition would be a fixed value over the course of vaporization. If this value were exactly $\text{UO}_{1.88}$, then only solid compositions of $\text{UO}_{1.88}$ would remain at this composition and all other compositions would diverge away from this composition. The experimental data indicate that all other compositions converge to this composition during evaporation. If the vapor composition were less than 1.88, all solid compositions between 1.88 and 2.0 would tend to increase in oxygen-to-uranium ratio which is contrary to experimental observations. These arguments indicate, therefore, that the $\text{UO}_{1.88}$ solid composition is single phase in the temperature region of 2200° to 2600°C . From phase-rule considerations, a single condensed phase enables the vapor composition to change during the course of evaporation so that the solid composition can converge to a single congruency composition within the single-phase region.

Studies on Urania Solid Solutions Containing Yttria

Compounds that have the fluorite lattice structure are frequently nonstoichiometric. Fluorite compounds such as UO_2 and ZrO_2 frequently can be made nonstoichiometric by heating at high temperatures in a low-oxygen partial pressure environment. These compounds can also be made nonstoichiometric by valence compensation using a third component. The latter method applied to UO_2 solid solutions containing Y_2O_3 produces oxygen-deficient structures at temperatures and oxygen pressures which are convenient for basic studies. As a result, urania solid solutions containing 40 to 50 mole percent Y_2O_3 were selected for kinetic and thermodynamic studies of a typical oxygen-deficient fluorite structure. The fluorite lattice is stable in this composition range for a variation in the oxygen-to-metal ratio from about 1.75 to 2.0.

The oxidation kinetic studies and oxygen self-diffusion measurements are nearly complete. The results obtained so far may be summarized as follows:

1. The oxygen self-diffusion coefficient measured by exchange of O^{18} with a urania solid solution of 40 mole percent Y_2O_3 is about the same as that which was reported by Belle* for UO_2 . The 40 mole percent composition exists as $(\text{U}, \text{Y})\text{O}_2$ in one-fifth atmosphere of oxygen, hence, the self-diffusion coefficient for oxygen does not appear to be appreciably changed by replacement of uranium and yttrium.
2. The oxidation of 50 mole percent composition after reduction in the presence of uranium metal at 950°C for 24 hours is similar to that of UO_2 reported by Anderson, et al.†

At liquid nitrogen temperatures, part of the oxygen uptake is caused by physical adsorption and is proportional to the pressure. Some irreversible chemical adsorption occurs. At -75°C , the physical adsorption is negligible, and the irreversible reaction which follows

*Belle, op. cit. pp.313-320.

†J. S. Anderson, L. E. J. Roberts, E. A. Harper, "The Oxides of Uranium, Part VII. The Oxidation of Uranium Dioxide," *Journal Chemical Society*, 1955, p. 3946.

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a logarithmic time dependence is dominant. Overnight annealing in vacuum at 300°C is sufficient to drive the chemisorbed layer of oxygen into random vacancy positions in the bulk material. After annealing at 300°C, the same amount of chemisorbed layer can be re-established on further oxidation at -75°C.

At -40°C and above, the oxidation follows a cubic rate law, changing to parabolic, and shows little or no pressure dependence. The onset of parabolic oxidation for a 50 mole percent composition occurs at temperatures which are considerably below that observed by Anderson, et al., for UO₂. This may be due to the large difference of free energy of reaction between the oxygen-deficient solid solution of UO₂ and nearly stoichiometric UO₂.

As the oxygen-to-uranium ratio becomes higher, the oxidation rate becomes slower. When the oxidation state of the 50 mole percent solution is near equilibrium with the oxygen pressure (70 microns), temperatures between 75° and 100°C are required for oxidation.

COMPATIBILITY OF UO₂ WITH REFRACTORY METALS

As a first step in determining the compatibility of UO₂ with refractory metals, it is necessary to determine how the oxygen-to-uranium ratio varies inside of a refractory-metal container under conditions which prevent weight loss. Stated differently, it must be determined if the urania stoichiometry changes during operation of a refractory-metal - urania fuel element. If a fuel element cladding is sufficiently nonporous, fuel loss by direct vaporization during extended heat treatment will be extremely small, but hydrogen in the external atmosphere may have free access to the fuel via diffusion through the matrix metal.

Cylindrical capsules of various metals were fabricated; each contained sintered samples of UO₂. 003. The UO₂ cylinders were sintered at 1700°C in dry hydrogen, then centerless-ground to fit the metal tubes with a few thousandths of an inch clearance on the diameter to accommodate differential thermal expansion. One end was sealed to the capsule, the UO₂ cylinder inserted, and the second end sealed in place. All closures were made by electron-beam welding in vacuum. Since the final seal was made in the presence of the oxide sample, a small gap was permitted between the end of the sample and the end plate. This gap amounted to about 5 percent of the total volume of the capsule. As additional protection for capsules made from 0.051-centimeter-thick metal, a double layer was used for the end sealed in place last. Thus far, capsules have been made of 0.051-centimeter rhenium, 0.051-centimeter powder metallurgy tantalum, and tungsten. The cylindrical wall of the tungsten capsule was 0.11 centimeter thick and the ends were 0.076 centimeter. After assembly, the capsules were leak-tested under 100 psi helium using a mass spectrometer.

Although contact between the metal and UO₂ was reasonably good, no attempt was made to produce a bond since urania vapor pressures are sufficiently high at the temperatures of interest that interaction rates between the UO₂ and metal container should be rapid. One capsule of each of the three materials was tested isothermally at 2400°C for 8 hours in flowing dry hydrogen. These capsules were approximately 1.3 centimeters in diameter and 1.5 centimeters in length, exposing about 9 cm² area of metal. Control runs with tungsten and rhenium specimens showed them to be completely stable with respect to weight change, but the weight of tantalum specimens with 9 cm² surface area increased at least several milligrams; this was ascribed to nitride formation from nitrogen impurities in the furnace gases. This interpretation is borne out by the X-ray diffraction identification of Ta₂N and a hardness data increase of the tantalum metal from about 325 to 675 DPH.

Data from these tests are summarized in Table 1.1-2. The tungsten- and rhenium-clad pellets were completely stable, showing no weight loss even though a leak was found in the tungsten-clad pellet after testing. The leak presumably developed during the cooling cycle,

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TABLE 1.1-2
ENCAPSULATED UO_2 .003 TESTED IN DRY HYDROGEN FOR 8 HOURS AT 2400°C

Capsule Material	Pre-Test Measurements					Post-Test Measurements			
	Metal Weight, g	UO_2 Weight, g	Total Weight, g	UO_2 Density, g/cm ³	Composite Density, g/cm ³	Total Weight, g	UO_2 Density, g/cm ³	Composite Density, g/cm ³	Oxygen-To- Uranium Ratio
Rhenium	11.2876	15.8454	27.1330	10.703	-	27.1328	10.858	12.358	2.001
Tantalum	8.5392	15.8101	24.3493	10.703	-	24.2267	10.828	10.233	1.863
Tungsten	14.2955	10.3186	24.6141	10.571	13.615	24.6142	10.892	13.631	2.001

or urania would have been lost. Polished sections of both the UO_2 and metal from these two capsules showed no apparent change from the pretest condition nor evidence of reaction at the area of contact. The UO_2 pellets were not bonded to the metal at any point and could be removed easily. Chemical analysis revealed that the oxygen-to-uranium ratio was essentially the same as before test.

The tantalum-clad pellet swelled at the ends and, as shown in the table, lost considerable weight. A post-test analysis of the urania showed an oxygen-to-uranium ratio of 1.86. A polished section revealed extensive precipitation of uranium metal in the urania. This precipitate was largely present at pores and grain boundaries, but generally appeared to be distributed uniformly and showed no gradients near the oxide - metal interface. The tantalum cladding showed evidence of some cracking, probably the result of nitriding, but there was no evidence of a leak before opening. The observed weight loss was consistent with the change in oxygen-to-uranium ratio on the assumption that only oxygen and no metal was lost to the system. Thickness measurements revealed no significant loss of tantalum and preliminary examination indicated no diffusion of uranium into the tantalum.

The explanation of this result has not been determined. It is clear that oxygen is escaping through the tantalum, probably via the intermediate of a lower oxide of tantalum. Whether hydrogen passing to the interior is involved in the reduction of UO_2 is not known. A parallel test in a rare gas will be necessary to answer this question. Whether the urania composition approaches a limiting oxygen-to-uranium ratio analogous to a congruent composition can be determined by running a series of tests of various durations. However, it has already been demonstrated that under conditions restraining the loss of UO_x vapors, the oxygen-to-uranium ratio in urania can change drastically by the preferential escape of oxygen through tantalum even if the actual weight loss is rather small in terms of percentage UO_2 . The significance of the above observation with respect to the operation of a Ta-clad W- UO_2 fuel element remains to be evaluated.

SUMMARY AND CONCLUSIONS

Studies of urania vaporization in flowing dry hydrogen have shown that limiting oxygen-to-uranium ratios of about 1.90, 1.88, and 1.87 are achieved at temperatures of 2200°, 2400°, and 2600°C, respectively. Composite samples of UO_2 plus uranium metal have been shown to homogenize quickly at these temperatures and, therefore, vaporization experiments can be properly performed with samples of UO_{2-x} made in this manner. Such tests have been run with x values up to 0.20. In all cases, vaporization has caused the oxygen-to-uranium ratio of the residual solid to change in the direction of the above limiting values. This observation together with phase-rule considerations is accepted as evidence that these limiting compositions represent congruency points and that, at temperature, the solid consists of a single phase.

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The limiting congruent compositions have also been shown to be extremely sensitive to moisture content (oxygen partial pressure). The moisture contents corresponding to the above congruent compositions have not been completely defined.

After testing in hydrogen at 2400°C for 8 hours, tungsten- and rhenium-clad sintered UO_2 specimens were found to have lost no weight and the urania remained unchanged at an oxygen-to-uranium ratio of 2.00. In a similar test, a tantalum-clad capsule lost nearly 1 weight percent of the urania. This loss is attributed exclusively to oxygen on the basis of the actual weights and the observed oxygen-to-uranium ratio of 1.86 after test.

Using Y_2O_3 additive to produce an oxygen-deficient lattice in UO_2 has shown that: (1) the oxidation rate becomes more rapid as the oxygen-to-metal ratio is lowered, (2) the onset of parabolic oxidation occurs at lower temperatures for an oxygen-deficient lattice than for nearly stoichiometric UO_2 , and (3) the oxygen self-diffusion coefficient is about the same in $\text{UO}_{2.67}$ - 40 mole percent Y_2O_3 as in UO_2 .

PLANS AND RECOMMENDATIONS

The most important problem in the physical chemistry study of urania is to obtain more detailed information concerning moisture content of the furnace atmospheres in the volatilization tests. This is of importance both with respect to mechanism of formation and composition of the vapor phase, and the effect of the moisture on resultant stoichiometry. This involves variables of flow rate, hydrogen partial pressure, and initial sample stoichiometry. After such relationships have been established, it will be possible to study the effect of temperature on the congruent vaporization as a separate variable.

In the compatibility studies, capsule tests will be continued to determine the effects of variations in time, temperature, initial urania stoichiometry, and thermal cycling. The matter of thermal cycling is particularly important since a decrease in temperature after a period at a higher temperature may cause metallic uranium to precipitate which, in turn, may react with other metals present. This study eventually will include the use of fuel additives such as ThO_2 .

Studies of 50 mole percent UO_{2+x} - Y_2O_3 solid solutions will be completed. These will include kinetics of oxidation and equilibrium oxygen pressure measurements over the pressure range of 0.1 to 1000 microns and over a temperature range of 300° to 950°C. Oxygen self-diffusion measurements in the solid solution will be continued.

1.2 $\text{UO}_{2.9} \cdot 3\text{Y}_2\text{O}_3$ FUEL MATERIAL (57065)

The objective of this task, which was terminated at the close of FY-63, was to evaluate the high-temperature capabilities of the UO_2 - UO_3 - Y_2O_3 system for nuclear reactor applications. The evaluation included a general study of the phase equilibria in the ternary system and a detailed investigation of the $\text{UO}_{2.9} \cdot 3\text{Y}_2\text{O}_3$ composition, the most refractory urania-bearing composition in the system.

A topical report,* being prepared for publication, describes this work fully; therefore, only a summary of the significant results achieved is presented in this report.

UO_2 - UO_3 - Y_2O_3 SYSTEM

Investigation of the UO_2 - UO_3 - Y_2O_3 ternary system produced a tentative phase diagram for temperatures up to 1700°C (Figure 1.2-1). Four phases have been identified in the

*J. F. White, E. F. Juenke, and D. R. Burgbacher, "The UO_2 - UO_3 - Y_2O_3 System and Evaluation of the $\text{UO}_{2.9} \cdot 3\text{Y}_2\text{O}_3$ Compositions," GE-NMPO, GEMP-263, (to be published).

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GE-NMPO

Fig. 1.2-1 – The UO_2 - UO_3 - Y_2O_3 ternary diagram from 1000° to 1700°C

system at temperatures between 1000° and 1700°C: (1) U_3O_8 , (2) face-centered cubic solid solution (FCC), (3) body-centered cubic (BCC) solid solution, and (4) a rhombohedral phase of the composition $\text{U}_m\text{Y}_{7-m}\text{O}_{12}$, where $m = 1.0$ to 3.4 . The rhombohedral phase oxidizes to a second rhombohedral phase with a nominal composition of $\text{U}_n\text{Y}_{8-n}\text{O}_{15}$ ($n = 2.0$ to 3.9) at temperatures below 1000°C. This latter phase transforms to a FCC phase after heating in air above 1000°C. The solubility of UO_2 in the BCC phase, which is about 14 mole percent between 1000° and 1700°C, decreases to zero as the uranium approaches the hexavalent oxidation state. The solubility of Y_2O_3 in the FCC solid solution ranges from zero to 50 mole percent Y_2O_3 under reducing conditions, and from 33 to 60 mole percent Y_2O_3 under oxidizing conditions at 1000°C.

At temperatures above 1000°C, the FCC solid solution is limited by a filled fluorite lattice of composition $(\text{U}, \text{Y})\text{O}_2$. However, oxidation at 300°C and below permits additional oxygen to be retained in the structure to a composition approaching $(\text{U}, \text{Y})\text{O}_{2.25}$.

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PREPARATION AND FABRICATION OF $\text{UO}_2 \cdot 9/3\text{Y}_2\text{O}_3$

Preparation of Powder

Early work on the mechanism and kinetics of forming $\text{UO}_2 \cdot 9/3\text{Y}_2\text{O}_3$ showed that the reaction between UO_2 and Y_2O_3 in air was complete in 24 hours at 1360°C . Subsequent studies on this reaction resulted in a process whereby the UO_2 and Y_2O_3 were mixed by milling for 30 minutes in a vibratory mill and then reacted for 8 hours at 1375°C in air. After reaction at this temperature, the material had an oxygen-to-uranium ratio of 2.98 to 3.0. The reacted material was milled for 4 hours in a vibratory mill which produced a sinterable powder with a surface area of 0.25 square meter per gram (measured by the BET method using Krypton gas). This reacted and milled $\text{UO}_2 \cdot 9/3\text{Y}_2\text{O}_3$ powder was then suitable for subsequent processing into test bodies by pressing or extruding.

Cold-Pressing

Bodies of simple shape, such as pellets and discs for thermal conductivity measurements, may be formed by dry-pressing in a steel die at 352 kg/cm^2 , followed by isostatic pressing at 1406 kg/cm^2 . The use of approximately 2 weight percent Mobilicer "R" wax* as a binder facilitated handling.

Extrusion and Coextrusion

A plastic dispersion mass of $\text{UO}_2 \cdot 9/3\text{Y}_2\text{O}_3$ was developed for cladding the inside surface of BeO hexagonal tubes by coextrusion to produce a fuel element of high specific-power potential. The best plasticizer developed was an aqueous solution of mixed polymers modified with glycerine. The polymers used were hydroxy-methyl cellulose (a strongly cross-linked polymer) and polyacrylamide (a linear chain polymer).

Dip-Coating

A procedure was developed for applying BeO cladding to the inside surface of BeO- $\text{UO}_2 \cdot 9/3\text{Y}_2\text{O}_3$ extruded tubes for the purpose of inhibiting fission product release during irradiation tests. This process was a dip-coating technique in which vibratory-milled BeO was suspended in water using approximately 1 weight percent ammonium alginate as a suspension-film forming agent. Vibratory milling of the BeO produced a finer powder and a more dense and more uniform coating.

Sintering

Milled $\text{UO}_2 \cdot 9/3\text{Y}_2\text{O}_3$ powder sinters to about 99.7 percent of theoretical density after 3 hours at 1750°C in an oxygen atmosphere. The grain size of this material is about 6 microns.

Sintering in a hydrogen atmosphere for about 12 hours at 1700°C produces a structure composed of the rhombohedral reduced phase plus a BCC phase. The density is about 99.1 percent of theoretical with an oxygen-to-uranium ratio of about 2.20. The grain size is about 3 microns. Subsequent oxidation of the hydrogen-sintered material raises the oxygen-to-uranium ratio to 2.9.

PHYSICAL PROPERTIES OF $\text{UO}_2 \cdot 9/3\text{Y}_2\text{O}_3$

Vapor Pressure

The vapor pressure of UO_3 evolving from $\text{UO}_2 \cdot 9/3\text{Y}_2\text{O}_3$ is low as compared to other uranium oxide bearing materials; the vapor pressure value at 1725°C is only 2×10^{-6} atmosphere. This is confirmed by tests where the UO_2 loss in air at 1700°C is negligible

* Registered trade-name, Mobil Oil Co.

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in 500 hours. Longer times at this temperature and correspondingly shorter times at higher temperatures results in detectable loss of uranium.

Reaction with BeO

As described above, under "Extrusion and Coextrusion," $\text{UO}_2 \cdot 9 \cdot 3\text{Y}_2\text{O}_3$ fuel was contained in BeO as a sandwich-type fuel element. This fuel element was found to be stable in air for 82 hours at 1600°C , i. e., above the BeO- Y_2O_3 eutectic which is at 1580°C , without evidence of any liquid being formed. This fuel element is, of course, stable without evidence of liquid formation for indefinite periods of time in air below 1580°C .

Other Physical Properties

Other properties of $\text{UO}_2 \cdot 9 \cdot 3\text{Y}_2\text{O}_3$ were measured and are summarized below:

1. The thermal expansion of $\text{UO}_2 \cdot 9 \cdot 3\text{Y}_2\text{O}_3$ is about the same as that of BeO: 0.65 percent at 800°C and 1.07 percent at 1200°C .
2. The thermal conductivity varies from 0.009 cal/sec-cm- $^\circ\text{C}$ at 750°C to 0.005 at 1950°C .
3. Electrical conductivity measurements show that $\text{UO}_2 \cdot 9 \cdot 3\text{Y}_2\text{O}_3$ is essentially an electronic conductor. The electrical conductivity was found to be 2.8×10^{-5} ohm $^{-1}$ cm $^{-1}$ at 300°C and 9×10^{-3} ohm $^{-1}$ cm $^{-1}$ at 1480°C with an activation energy of 0.80 ev.
4. The heat capacity can be expressed as:

$$C_p = 0.101 + 11.94 \times 10^{-6} T + 8.94 \times 10^{-9} T^2$$
5. The room-temperature values for the modulus of rupture and the modulus of elasticity of $\text{UO}_2 \cdot 9 \cdot 3\text{Y}_2\text{O}_3$ are about 985 kg/cm 2 and 1.72×10^6 kg/cm 2 , respectively. The above modulus-of-rupture strength is about the same as the room-temperature strength of UO_2 . It should be noted that the modulus of rupture of $\text{UO}_2 \cdot 9 \cdot 3\text{Y}_2\text{O}_3$ increases by about 18 percent at 1500°C , whereas the modulus of elasticity decreases uniformly by about 16 percent over the temperature range up to 1500°C .
6. This fine-grained material has high resistance to compressive creep at high temperatures as compared to BeO of similar grain size. The creep after 100 hours at 1540°C under a load of 8.8 kg/cm 2 was 0.43 percent, and under a load of 17.6 kg/cm 2 was 0.50 percent.

IRRADIATION TESTING

A cursory test, run on an encapsulated sample of $\text{UO}_2 \cdot 9 \cdot 3\text{Y}_2\text{O}_3$, showed that the material did not fracture nor otherwise fail after a dose of about 10^{20} nvt ($E_n \geq 1$ Mev) at a temperature of 400°C . More detailed irradiation testing of this material is being conducted under Job 57068, "Burnup Capabilities of Y_2O_3 -Stabilized UO_2 and Stabilized Fuel - BeO Matrix Materials," and is reported in section 3.1 of this volume.

SUMMARY AND CONCLUSIONS

The results of this evaluation program indicated that $\text{UO}_2 \cdot 9 \cdot 3\text{Y}_2\text{O}_3$ fuel compositions show promise for application in reactor systems operating for several thousand hours at temperatures up to 1700°C .

This composition is the only known fuel material with such a temperature capability which can operate in both oxidizing and reducing atmospheres, and which can be cycled between oxidizing and reducing atmospheres without catastrophic changes in strength or physical integrity.

For high specific-power reactor applications, the $\text{UO}_2 \cdot 9 \cdot 3\text{Y}_2\text{O}_3$ fuel composition shows promise as an internal fuel cladding on tubular BeO fuel elements.

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1.3 HIGH-TEMPERATURE CARBIDES AND BORIDES RESEARCH (57073)

The objective of this study is to determine the physico-chemical properties of high-melting carbides and borides and to define the stability of the materials in high-temperature gaseous environments.

Initial studies under this task, which was begun in July 1963, are intended to determine, in a general yet quantitative way, the evaporation characteristics of the refractory-metal carbides and borides in gaseous environments.

LITERATURE SEARCH

A review of the literature on the vaporization characteristics of the zirconium-carbon system was conducted. An analysis of the published data* indicated that all experimental data are consistent with a congruent vaporization composition of $\text{ZrC}_{0.85}$, or 46 atomic percent carbon in vacuum and inert atmospheres.

To determine the areas of interest and general approach of other investigators engaged in carbide and boride research, a general survey of the literature was undertaken.† This survey revealed a general lack of fundamental information on the high-temperature chemistry of carbide and boride systems and their vaporization characteristics in gaseous environments. The aim of the current GE-NMPO work, therefore, is to develop a greater understanding of the fundamental behavior of the carbides and borides in gaseous environments and to evaluate their potential use as high-temperature nuclear fuel elements and structural members.

SAMPLE PREPARATION

The experimental program to date has resulted in: (1) construction of furnaces and handling facilities for preparation of pure materials, (2) evaluation of potential materials for use as containers and other furnace fixtures, and (3) preliminary sintering studies on commercially available materials.

Commercially available powders of ZrC , TiC , TaC , and HfC were obtained for initial sintering and evaporation studies. Chemical analyses of the as-received powders established the major impurities (Table 1.3-1). X-ray diffraction analyses of HfC and ZrC powders show each to be single-phase, face-centered cubic with lattice parameters of 4.64 Å and 4.692 Å, respectively. The lattice parameters for the ZrC phase are consistent with those reported by Norton and Lewis‡ for the equivalent composition ($a_0 = 4.694$ Å), but appreciably below the values reported by Sara, et al.§ ($a_0 = 4.702$ Å). The lattice parameter for the HfC is consistent with the published values ($a_0 = 4.64$ Å).•

Test specimens were prepared from -325 mesh powder in the form of pellets 1.27 centimeters in diameter and 1.27 to 1.90 centimeters long. One weight percent polyvinyl alcohol was added as a binder. The pellets were presintered by heating to approximately

*"High-Temperature Materials Program Progress Report No. 30, Part B," GE-NMPO, GEMP-30B, December 31, 1963, p. 41.

†E. F. Juenke, "A Review of Recent Research on Refractory Carbides and Borides," GE-NMPO, GEMP-267, to be published.

‡J. T. Norton and R. K. Lewis, "Final Report, Properties of Non-Stoichiometric Metallic Carbides," (Contract NASR-98) Advanced Metals Research Corp., March 29, 1963.

§R. V. Sara, C. E. Lowell, R. T. Dolloff, "Research Study to Determine the Phase Equilibrium Relations of Selected Metal Carbides at High Temperatures," WADD-TR-60-143 Part IV, February 1963.

•E. K. Storms, "A Critical Review of Refractories Part I, Selected Properties of Group 4a, -5a, and -6a Carbides," LAMS-2674, February 1, 1962.

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TABLE 1.3-1
CHEMICAL ANALYSIS OF CARBIDE POWDERS
Impurities,^a wt %

	ZrC	TiC	TaC	HfC
Si	0.05-0.5	<0.01	0.01-0.10	<0.01
Al	b	<0.01	<0.01	<0.01
Fe	<0.01	<0.01	0.01-0.10	0.05-0.5
Ti	0.05-0.5	b	0.005-0.05	0.005-0.05
Cu	<0.01	<0.01	<0.01	<0.01
Ni	0.005-0.05	<0.01	<0.01	<0.01
Cr	0.005-0.05	0.05-0.5	0.005-0.05	<0.01
V	b	0.05-0.5	b	b
Mn	b	b	0.005-0.05	b
Ca	<0.01	<0.01	<0.01	<0.01
Mg	b	<0.01	<0.01	<0.01
Zr	b	<0.01	<0.01	0.5-5.0
Mo	0.05-0.5	<0.01	<0.01	<0.01
Co	0.005-0.05	0.01-0.10	0.005-0.05	b
B	0.005-0.05	b	b	0.005-0.05
Nb	b	b	0.5-5.0	0.05-0.50
W	0.01-0.10	0.05-0.50	0.05-0.50	b
O	0.244	0.519	0.317	-

^aThe elements Bi, Pb, Sm, Ag, Sb, As, Zn, Ba, Sr, Na, K, Li, and Cd were not detected in any of the powders.

^bNot detected.

1400°C in hydrogen to remove most of the binder and to permit them to densify sufficiently to allow further handling without loss of powder. Weight loss measurements, coupled with chemical analyses of the material before and after sintering, permit evaluation of the removal of volatile components during the sintering experiments.

Pellets of HfC and ZrC, prepared as described above, were sintered in both vacuum ($\sim 10^{-5}$ Torr) and helium at temperatures between 2000°C and 2200°C. Metallographic examination of polished sections indicates a porosity of about 10 to 20 percent in specimens prepared under these conditions. Chemical analyses are being performed to determine the relative purity of the samples after preparation. Initially, tantalum was used as the susceptor in the induction sintering furnace, and for suspending the sample in the furnace. However, because tantalum caused contamination of the pellet surfaces, rhenium was chosen for the susceptor material for induction heating and for the container material for resistance heating. No contamination effects from rhenium have been observed at temperatures up to 2200°C.

VAPORIZATION STUDIES ON ZIRCONIUM CARBIDE

Zirconium carbide pellets, sintered in vacuum at temperatures between 2000°C and 2100°C, were heated in flowing hydrogen (flow rate of 0.5 to 2.0 liters per min., and a dewpoint of approximately -46°C) for periods of from 1 to 4 hours. The specimens were weighed after each treatment and heating was continued until two successive readings differed by less than 1.0 milligram. The experiments were carried out at temperatures of 1500°C, 1650°C, 2000°C, and 2100°C. The X-ray data in Table 1.3-2, taken after the various treatments, indicate a consistent increase in lattice parameter with temperature rise. Table 1.3-3 gives the analytical results from chemical analyses performed on the specimens heated at 1500°C and 2000°C, and presents analyses of the starting powder and of an as-sintered pellet for comparison of carbon content after the various treatments. Obviously, the increase in total carbon content during sintering is caused by the decom-

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TABLE 1.3-2
X-RAY DIFFRACTION ANALYSES OF ZrC
AFTER VARIOUS HEAT TREATMENTS

Treatment	Lattice Parameter (a_0), Å
As-received powder	4.692
Sintered 30 minutes at 2000°C, vacuum	4.694
Heated 13 hours at 1500°C in H ₂	4.690
Heated 9 hours at 1650°C in H ₂	4.692
Heated 2 hours at 2000°C in H ₂	4.693
Heated 2 hours at 2100°C in H ₂	4.694
Heated 6 hours at 2100°C in H ₂	4.695

TABLE 1.3-3
ANALYSES FOR TOTAL AND UNCOMBINED CARBON IN ZrC
AFTER VARIOUS HEAT TREATMENTS

	As-Received Powder	Heat Treatment		
		30 Minutes At 2000°C In Vacuum	13 Hours At 1500°C In H ₂	2 Hours At 2000°C In H ₂
Zirconium, wt %	88.03	87.90	88.22	89.11
Total carbon, wt %	10.70	11.31	10.55	10.20
Free carbon, wt %	1.17	0.69	0.27	0.06
C-to-Zr ratio for combined carbon	0.82	0.92	0.89	0.86

position of the organic binder, which was not removed from the material in the 30-minute vacuum sintering treatment at 2000°C. These data also indicate that the combined carbon in the starting material is significantly less than the stoichiometric carbon-to-zirconium ratio of 1:1. The carbon-to-zirconium ratio for combined carbon in the as-received material is 0.82. The treatment at 2000°C for 30 minutes increased the carbon-to-zirconium ratio for combined carbon to 0.92. Heating in hydrogen for 13 hours at 1500°C reduced this ratio to 0.89. Heating at 2000°C for 2 hours reduced the carbon-to-zirconium ratio to 0.86. In this temperature range, the carbon could be removed by either of two reactions: $C + H_2O = CO + H_2$, or $2C + H_2 = C_2H_2$.

With starting pressures of 1 atmosphere H₂ and 6×10^{-5} atmosphere H₂O, the equilibrium pressures of CO and C₂H₂ at 2000°C are 6×10^{-5} and 1.5×10^{-2} atmosphere, respectively. On the basis of equilibrium, the reaction $2C + H_2 = C_2H_2$, therefore, appears to account for the bulk of carbon removal from the sample, and is not materially affected by the moisture in the hydrogen. The data indicate that the free-carbon* contents are reduced in ZrC by heating in hydrogen at temperatures of 1500°C and 2000°C.

*Free carbon is defined as the carbon insoluble in HF and HNO₃.

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SUMMARY AND CONCLUSIONS

Vacuum sintering of ZrC pellets for 30 minutes at 2000°C in the presence of an organic binder results in an increase in both total and combined carbon content.

Hydrogen treatment of substoichiometric ZrC for 13 hours at 1500°C and 2 hours at 2000°C results in combined carbon-to-zirconium ratios of 0.89 and 0.86, respectively. Nearly all free carbon is removed in 2 hours at 2000°C.

There is an apparently consistent increase in the lattice parameter of the FCC ZrC solid solution with increasing temperature of the hydrogen treatment. It has yet to be established whether this effect is related to volatilization of impurities, changes in stoichiometry, or free-carbon content.

PLANS AND RECOMMENDATIONS

Materials preparation and fabrication studies to attain high-purity and high-density specimens will be continued.

Preliminary evaluation of vaporization characteristics, in hydrogen atmospheres between 2000° and 2500°C, of the commercially available monocarbides and diborides of Ta, Zr, Hf, Ti, U, and Th will be completed.

Vaporization tests on samples prepared with pure materials will be conducted to determine the effects of atmosphere and temperature upon congruent vaporization composition.

Experiments will be continued to establish the causes of an apparent consistent increase in lattice parameter of the FCC ZrC phase with increased temperature of hydrogen treatment.

1.4 COATED FUEL PARTICLE DEVELOPMENT AND EVALUATION (57064)

The objective of this program is the preparation of small coated fuel particles and their incorporation in various matrices to yield a dispersion-type fuel element in which fuel - matrix reactions, fuel - coolant reactions, and fission product release are inhibited at temperatures to at least 1650°C.

Work during Calendar Year 1963 consisted of preparing spherical F-204 (45UO₂ - 35.6Y₂O₃ - 19.4ZrO₂)* particles approximately 50 microns in diameter, coating them with an oxide by a vapor deposition process, incorporating the spheres (both uncoated and coated) in a BeO matrix, and determining the irradiation stability and fission product retention of the fueled ceramic bodies.

PREPARATION OF SPHERICAL FUEL PARTICLES

Small, dense fuel particles are needed for dispersion in fuel elements with high surface-area-to-volume ratios; they must be of high sphericity to provide a uniform coating surface. To make fuel particles possessing these qualities, solid-solution UO₂-Y₂O₃-ZrO₂ powders with enough excess fuel to compensate for fuel loss during spheroidization were prepared and spheroidized in a direct-current plasma flame.

Preparation of Starting Powders

Powders of UO₂, Y₂O₃, and ZrO₂, all less than 44 microns in diameter, were processed as reported earlier† to yield inhomogeneous face-centered cubic (FCC) solid solution com-

*All compositions are in weight percent unless otherwise noted.

†"Second Annual Report - High-Temperature Materials and Reactor Component Development Programs, Volume II - Materials," GE-NMPO, GEMP-177B, February 28, 1963, p. 127.

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pacts containing a trace of an unidentified minor phase. These compacts were then comminuted to powder in the 37- to 62-micron size range. The initially prepared compacts were quite friable and yielded a higher fraction of fines (particles less than 37 microns in diameter) during comminution than compacts prepared by re-pressing and refiring the fines.

Studies of various comminution methods revealed that a high-energy method (hammer mill) resulted in yields of less than 10-percent powder in the usable size range. On the other hand, all low-energy methods (hand grinding, rod mill, and roll crusher) resulted in essentially equal yields, approximately 20 percent for comminution of the original fired compacts and approximately 40 percent for comminution of compacts obtained from re-pressed and refired fines. Comminution was easiest and fastest with the roll crusher. Photomicrographs of the internal and external appearance of F-215 ($60\text{UO}_2 - 25.9\text{Y}_2\text{O}_3 - 14.1\text{ZrO}_2$) powder comminuted using the roll crusher are shown in Figure 1.4-1.

Spheroidization of Fuel Powders

Most of the spheroidization work was done with the direct-current plasma apparatus using powders in the 37- to 62-micron size range. Procedures were developed to remove plasma-treated particles that were not spherical or that contained large voids by an air elutriation apparatus and an inclined plane apparatus.

Improved control and reproducibility were obtained with a new plasma torch.* With the new torch, spheroidization of F-215 powders in the 37- to 62-micron size range was achieved at (1) power settings of 37 volts and 430 amperes, (2) a plasma gas flow of 1700 liters per hour of helium and 142 liters per hour of argon, (3) a particle-carrier gas flow of 170 liters per hour of argon, and (4) a powder feed rate of 400 grams per hour from a hopper feeder.† Photomicrographs of the internal and external appearance of F-204 spheres produced with the new plasma torch and culled by air elutriation and inclined plane separation are shown in Figure 1.4-2.

A new particle collector system, Figure 1.4-3, was installed for use with the direct-current plasma apparatus. Advantages of this system over the one used previously are (1) sight ports allow direct observation of the plasma flame, (2) spheres are collected in a controlled atmosphere, and (3) the length of the collector chamber can be changed for processing materials over a wide range of cooling rates.

In preparation for the first series of irradiation tests, approximately 250 grams of enriched F-204 spheres were prepared by spheroidization of F-215 powder in the direct-current plasma flame and culled by air elutriation. The particles ranged from 25 to 55 microns in diameter. The average composition, determined by chemical analysis, was $45.02\text{UO}_2 - 36.38\text{ZrO}_2 - 18.60\text{Y}_2\text{O}_3$. X-ray diffraction analysis showed a single-phase FCC structure with $a_0 = 5.28 \text{ \AA}$. Electron microprobe examination of similar spheres from another lot showed that the UO_2 content varied by several percent from sphere to sphere, but no gradients of fuel concentration were observed within a given sphere. Studies made after preparation of the enriched F-204 spheres revealed that variation in fuel content from sphere to sphere can be decreased by decreasing the size range of particles fed to the plasma in a given run.

A brief series of experiments revealed that particles containing an unreacted mixture of UO_2 , Y_2O_3 , and ZrO_2 in the F-215 composition are converted to single-phase FCC spheres in the plasma flame but are inhomogeneous in composition within the phase. Because of this inhomogeneity, spheroidization tests with unreacted powders were discontinued.

* Model U-51, Thermal Dynamics Corporation, Hanover, New Hampshire.

† Model P1-100, Thermal Dynamics Corporation, Hanover, New Hampshire.

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Neg. 3417

UNETCHED

250 X

Neg. 3546

100 X

Fig. 1.4-1 — Photomicrographs of F-215 ($60\text{UO}_2 - 25.9\text{Y}_2\text{O}_3 - 14.1\text{ZrO}_2$) powder as comminuted in the roll crusher

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Neg. 3654

UNETCHED

250 X

Neg. 3549

100 X

Fig. 1.4-2—Photomicrographs of F-204 ($45\text{UO}_2 - 35.6\text{Y}_2\text{O}_3 - 19.4\text{ZrO}_2$) spheres produced in the direct current plasma flame and culled by air elutriation and inclined plane separation

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Fig. 1.4-3 - Particle collector system for direct-current plasma apparatus (AS-219)

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Preliminary experiments with a small 7.5-kilowatt radio-frequency induction generator* showed that spheres of greater uniformity and higher density could be obtained in an inductively coupled plasma; therefore, a 50-kilowatt induction generator is being modified to deliver power at radio frequency. A Bausch and Lomb 1.5-meter grating spectrograph was obtained to measure inductively coupled plasma temperatures for control purposes.

COATING OF SPHERICAL FUEL PARTICLES

Fuel spheres in approximately the 35- to 55-micron size range were coated with Y_2O_3 -stabilized ZrO_2 or with BeO by vapor reaction processes carried out in the spirally agitated fluidized bed shown in Figure 1.4-4. The oxides were obtained by reacting the appropriate metal chlorides with water produced by the H_2 - CO_2 reaction in the hot region of the coating apparatus. For coating fuel particles with Y_2O_3 -stabilized ZrO_2 , the $ZrCl_4$ gas was produced by reacting dry HCl gas with Zr wire; the YCl_3 gas was obtained by transpiration from a YCl_3 container located near the hot region of the coating apparatus. For coating fuel particles with BeO, the $BeCl_2$ gas was formed by reacting dry HCl gas with Be turnings. The amount of transported YCl_3 varied by less than 3 percent over four separate coating runs; the rates at which $ZrCl_4$ or $BeCl_2$ were produced could be controlled by controlling the HCl flow rate.

Photomicrographs of the internal and external appearance of F-204 spheres coated with Y_2O_3 -stabilized ZrO_2 in the spirally agitated coating apparatus are shown in Figure 1.4-5. The coatings contain 24 weight percent Y_2O_3 and are single-phase FCC in structure.

F-204 spheres were coated with BeO at 1100°C in the spirally agitated coating apparatus. Table 1.4-1 gives a comparison between BeO-coated and uncoated F-204 spheres when tested in air under the same conditions. The weight increase of the coated fuel occurs by diffusion of oxygen through the BeO coating and oxidation of the fuel to a higher oxidation state. The uncoated sphere is completely oxidized in a few minutes at 1230°C, while the oxidation rate of the BeO-coated sphere is slower, indicating that the BeO layer is impermeable to oxygen except by diffusion. The brief initial weight loss (~0.20%) of the coated spheres is probably caused by loss of volatile materials remaining on the coating from the washing operation. Both uncoated and coated spheres show a gradual loss from volatilization of UO_3 after oxidation to the highest nonvolatile oxidation state is complete. The coated spheres were not affected by thermal cycling or by pretreatment at 800°C. Figure 1.4-6 shows photomicrographs of 60-micron spheres with 12 microns of coating, as-coated, and after testing at elevated temperatures. It can be seen that the as-deposited coating was quite dense and that some grain growth occurred in the coating during testing.

INCORPORATION OF SPHERICAL FUEL PARTICLES IN A BeO MATRIX

Fueled spheres (uncoated, coated with Y_2O_3 -stabilized ZrO_2 , or coated with BeO) were incorporated into BeO matrices, and the resulting mixtures were extruded and sintered. Some of the sintered bodies were coated with Y_2O_3 -stabilized ZrO_2 in a vapor reaction process.

In preparation for the first series of irradiation tests, enriched F-204 spheres were incorporated into a BeO matrix to yield extruded and sintered hexagonal tubes that were 0.775 centimeter acrossflats, 0.551 centimeter in internal diameter, and 11.25 centimeters long. As shown in Table 1.4-2, the tubes containing F-204 spheres were inferior in strength and fuel retention to similar tubes fueled with impact-milled F-204 powder. The larger matrix grain size for the tubes containing spherical fuel accounted in part for their lower modulus-of-rupture strength. As explained later, matrix grain growth can be inhibited by the presence of small amounts of ZrO_2 sol. The cause for the relatively high fuel loss in the F-204

*"Second Annual Report—High-Temperature Materials and Reactor Component Development Programs, Volume II—Materials," GE-NMPO, GEMP-177B, February 28, 1963, pp.127-129.

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Fig. 1.4-4—Spirally agitated bed apparatus for coating fuel spheres with Y₂O₃-stabilized ZrO₂ (resistance heating) (AS 238)

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Neg. 3566

ETCHED IN 20% HF

250 X

Neg. 3547

100 X

Fig. 1.4-5—Photomicrographs of F-204 spheres coated with Y_2O_3 -stabilized ZrO_2

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TABLE 1.4-1
ELEVATED TEMPERATURE TESTING OF FUEL SPHERES

Parameter	Uncoated Spheres	Coating Run	
		CR-53	CR-56
F-204 sphere diameter, microns	37-44	60 ^a	37 ^a
BeO coating thickness, microns	-	12	4.5
UO ₂ content, wt %	45	25	38
Weight Change, % of UO ₂ (all values cumulative)			
Low temperature treatment ^b	+1.67	-0.20	-0.19
Thermal cycling ^c	+0.93	-0.31	-0.11
Oxidation testing at 1230°C			
1 hr	+1.41	-0.23	-0.20
2 hr	+1.39	-0.17	-0.17
3 hr	+1.40	-0.01	0.00
4 hr	+1.41	+0.12	+0.17
5 hr	+1.39	+0.11	+0.33
48 hr	+1.06	+1.53	+1.95
72 hr	+0.89	+1.60	+1.79
141 hr	+0.45	+1.17	+1.29
329 hr	-0.80	-0.52	-0.21
500 hr	-1.64	-1.70	-1.30

^aAverage.

^bIn air for 1 hour at 800°C.

^cFive thermal cycles from room temperature to 1230°C, 10 minutes dwell time at each temperature.

TABLE 1.4-2
COMPARISON OF PROPERTIES OF SINTERED 6BF-204 TUBES^a
CONTAINING F-204 AS SPHERES AND AS POWDER

Property	Fuel	
	F-204 Spheres	Impact-Milled F-204 Powder
Density, percent of theoretical	97.3	98.5
Range of fuel particle size (as added to BeO), microns	37-53	All less than 44; half of total less than 16
Matrix grain size, microns	28	11
Modulus of rupture, ^b kg/cm ²	1600	2300
Fuel loss (150 hr at 1510°C in air), wt % of UO ₂	2.5	0.6

^aExtruded and sintered BeO tubes containing 6 weight percent UO₂ added as the composition F-204.

^bAverage for five tubes at room temperature.

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Neg. 3735

UNETCHED
AS-COATED

250 X

Neg. 3763

UNETCHED

250 X

AFTER TESTING IN AIR FOR 66 HRS AT 1230°C, 25 HRS AT
1370°C, AND 16 HRS AT 1510°C

Fig. 1.4-6—Photomicrographs of F-204 spheres coated with BeO at 1100°C

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spheres is not fully known, but it is probably related to the higher concentration of fuel exposed at the surface of the sintered body, as shown in Figure 1.4-7. When a fuel sphere is at the surface, it has a much larger reservoir of UO_2 than does the finer dispersion; this larger reservoir would lead to relatively higher fuel losses until the surface fuel is depleted of uranium.

Fig. 1.4-7—Photograph of external surface of a sintered BeO tube containing F-204 spheres (Neg. P63-5-6a)

An earlier study* showed limited diffusion of fuel from a 6BF-116† tube into a coextruded Y_2O_3 -stabilized ZrO_2 cladding during 1000 hours at 1540°C in air having a dewpoint of -65°C . To determine if the limited diffusion shown in this earlier test would also be observed in F-204 spheres with Y_2O_3 -stabilized ZrO_2 cladding, these spheres were incorporated into a BeO matrix; the resulting mixture was extruded and sintered for 2 hours at temperatures of 1400° , 1480° , 1565° , 1620° , and 1680°C in hydrogen having a dewpoint of 0°C . As shown in the photomicrographs in Figure 1.4-8, interdiffusion between the coating and the fuel core was negligible at 1480°C but extensive at 1680°C . Interdiffusion at 1565°C and 1620°C over the same period of time was detectable but less severe than at 1680°C . These results showed that the maximum sintering temperature for a BeO body containing F-204 spheres coated with Y_2O_3 -stabilized ZrO_2 should be approximately 1500°C for 2 hours; however, as shown in Figure 1.4-8, sintering near this temperature does not yield high matrix density.

Interdiffusion of the fuel with the BeO coating and the BeO coating with the matrix was also studied. Photomicrographs of extruded BeO bodies containing BeO-coated F-204 spheres sintered at 1620°C and 1680°C are shown in Figure 1.4-9a. It can be seen that

*A. J. DeLai and J. F. White, "Fuel Loss From Ceramic Fuel Elements," GE-NMPO, APEX-688, September 1961.

†F-116 ($45\text{UO}_2 - 55\text{Y}_2\text{O}_3$) fuel in a BeO matrix to give a fuel loading of 6 weight percent UO_2 .

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Neg. 3917

250 X

POLARIZED LIGHT
SINTERED AT 1480°C

Neg. 3657

250 X

ETCHED IN 20% HF
POLARIZED LIGHT
SINTERED AT 1680°C

Fig. 1.4-8—Photomicrographs of extruded BeO bodies containing F-204 spheres coated with Y_2O_3 -stabilized ZrO_2 and sintered in hydrogen having a dewpoint of 0°C

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Neg. 3765

250 X

SINTERED AT 1620°C
AVERAGE GRAIN SIZE - 28 MICRONS

Neg. 3766

250 X

SINTERED AT 1680°C
AVERAGE GRAIN SIZE - 49 MICRONS

a. BeO-COATED F-204 SPHERES IN A BeO MATRIX

Neg. 3853

250 X

SINTERED AT 1620°C
AVERAGE GRAIN SIZE - 5 MICRONS

Neg. 3854

250 X

SINTERED AT 1680°C
AVERAGE GRAIN SIZE - 15 MICRONS

b. BeO-COATED F-204 SPHERES IN A BeO - 2ZrO₂ (WEIGHT PERCENT) MATRIX

Fig. 1.4-9 - Photomicrographs of extruded and sintered bodies containing BeO-coated F-204 spheres sintered in hydrogen (dewpoint of 0°C) and etched in 20% HF

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there is little porosity in the BeO near the fuel cores; however, the coating grains appear to have grown into the BeO matrix during sintering, especially at 1680°C.

Matrix grain growth and, to a lesser extent, growth of coating grains into the matrix were inhibited by adding 2 weight percent ZrO_2 , as a sol, to an extrusion mix containing BeO-coated F-204 spheres in BeO. Figure 1.4-9b shows photomicrographs of sintered rods, 0.25 centimeter in diameter, which contain ZrO_2 sol. The modulus-of-rupture strength for these rods was 1810 kg/cm², a value greater than that reported in Table 1.4-2 for hexagonal BeO tubes containing F-204 spheres without ZrO_2 sol.

IRRADIATION TESTING

Post-irradiation examination was completed of tubes from a LITR irradiation test (LTC-67A) described previously.* In the as-sintered condition, the average modulus of rupture of these specimens was 2420 kg/cm²; after irradiation the strength was 2380 kg/cm². The pre-test specimens contained an average of 5.95 percent UO_2 ; post-test analysis showed 5.84 percent UO_2 . This difference in fuel content is attributed to fuel burnup. The fractional release (R/B) of fission products is shown in Figure 1.4-10; it is in fair agreement with what was expected from direct recoil data, i. e., 1 to 3 x 10⁻⁴.

Fig. 1.4-10 - Comparison of fractional release values (R/B) for in-pile tests LTC-67A, LTC-67B, and LTC-69

* "Second Annual Report - High-Temperature Materials and Reactor Component Development Programs, Volume II - Materials," GE-NMPO, GEMP-177B, February 28, 1963, pp. 86-88.

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Uncoated F-204 spheres incorporated into a BeO matrix were subjected to irradiation testing in the C-48 facility of the LITR in two separate tests, LTC-67B and LTC-69. Test LTC-67B contained unclad fueled tubes; test LTC-69 contained fueled tubes with vapor-deposited Y_2O_3 -stabilized ZrO_2 cladding. The test conditions are summarized in Table 1.4-3. Physical integrity of the fueled tubes and the coating was maintained during irradiation testing.

TABLE 1.4-3
LITR TEST PROGRAM FOR FUELED BeO^a

Test Number	Cladding ^b		Specimen Size, cm	Test Time, hr	Test Temperature, °C
	On Fuel Particle	On Substrate			
LTC-67A	None	None	0.754 by 0.513 by 11.25	1475	1260
LTC-67B	None	None	0.775 by 0.551 by 11.25	504	1230
LTC-69	None	ZrO_2^c	0.777 by 0.546 by 11.28	552	1230
LTC-70	BeO	None	In process	-	-
LTC-71	BeO	ZrO_2	In process	-	-

^aExtruded hexagonal external configuration tubes of Brush UOX-grade BeO fueled with 6 weight percent UO_2 (93.2 percent U^{235}) added as the F-204 composition, $45UO_2 - 35.6Y_2O_3 - 19.4ZrO_2$ (wt %). All tubes were sintered for 2 hours at $1675^\circ C$ in H_2 (having a dewpoint of $0^\circ C$) to at least 97.5 percent of theoretical density. Fuel in these compositions was added as spheres in the size range -270/+500 mesh (approximately 25 to 53 microns) for all tests except No. LTC-67A. Fuel for the tubes used in test No. LTC-67A was added as impact-milled F-204 powder with an average particle size of 4 to 5 microns.

^bVapor-deposited cladding.

^c Y_2O_3 -stabilized ZrO_2 .

In-Pile Measurement of Fission Product Release

Test LTC-69 - Test LTC-69 consisted of six BF-204 tubes containing spheroidized fuel particles; each tube was fully clad with 0.025 millimeter of vapor-deposited Y_2O_3 -stabilized ZrO_2 .^{*} The test was operated for a total of 552 hours at a maximum indicated temperature of $1230^\circ C$ in air having a dewpoint of $-40^\circ C$.

Fractional release data were obtained for Kr^{85m} , Kr^{87} , Kr^{88} , Xe^{133} , Xe^{135} , and I^{131} as shown in Table 1.4-4. The off-gas ducting from this test was leached to determine the amount of deposited I^{131} ; the I^{131} release, determined from the carbon traps, was then corrected for the deposition and the corrected values are listed in the table.

Previous experience[†] with coated fuel elements indicated that a temperature change, due to reactor shutdown and startup, caused a large transient release of I^{131} . This release affected the R/B values for as long as 25 to 50 hours after the temperature change; however, the magnitude of the transient release is dependent upon the concentration of the particular isotope as indicated by the short-lived Kr^{89} (half life = 3.2 minutes) R/B values, which were not affected by a temperature change. Thus, the R/B values shown in Table 1.4-4 for the gases from traps C-1 and C-2, for Xe^{133} from trap C-7, and for I^{131} from trap B-1 are not representative of the steady-state release. The indicated R/B values were obtained too soon after a temperature change to be representative of steady-state release.

^{*}"High-Temperature Materials Program Progress Report No. 24, Part B," GE-NMPO, GEMP-24B, June 28, 1963, pp. 9-10.

[†]J. T. Bittel, "Evaluation of High Density Vapor Deposited ZrO_2 Coatings on $BeO-UO_2-Y_2O_3$ Fuel Elements," GE-ANPD, DC 61-3-150, March 30, 1961, p. 22.

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TABLE 1.4-4
FISSION PRODUCT RELEASE FROM TEST LTC-69
OPERATED AT 1230°C

Trap Number	Time At Temperature, hr	Fractional Release (R/B), ^a 10 ⁻⁴					
		Kr ^{85m}	Kr ⁸⁷	Kr ⁸⁸	Xe ¹³³	Xe ¹³⁵	I ¹³¹
C-1	0.2	2	1	2	0.01 ^b	0.07 ^b	-
C-2	2.3	2	0.7	0.6	0.03 ^b	0.02 ^b	-
B-1	3.0	-	-	-	-	-	9 ^c
C-3	42.6	1	0.4	0.7	0.4 ^b	0.6	-
B-2	43.0	-	-	-	-	-	4 ^c
C-4	114.5	0.6	0.3	0.6	1	0.5	-
Shutdown	136.7						
Shutdown	173.9						
C-5	198.2	0.5	0.2	0.6	2	0.4	-
C-6	293.6	0.3	0.5	0.5	1	0.5	-
Shutdown	294.2						
Shutdown	335.3						
B-3	356.7	-	-	-	-	-	3 ^c
Shutdown	378.5						
Shutdown	385.7						
C-7	393.4	0.4	0.2	0.4	6	0.3	-
Shutdown	443.2						
C-8	488.4	0.4	0.3	0.4	1	0.4	-
B-4	489.3	-	-	-	-	-	3 ^c
End of Test	552.3	-	-	-	-	-	-

^aFractional release is defined as the ratio of the atoms released from the test specimens per second to the equilibrium production rate (sec⁻¹).

^bThese values, when corrected for the difference between true production rate and equilibrium production rate, gave R/B values comparable to those obtained for the other noble gas isotopes.

^cValues corrected for a line deposition of 54 percent.

The remainder of the data in the table indicate that the R/B values for Kr⁸⁷, Kr⁸⁸, Kr^{85m}, and Xe¹³⁵ were from recoil; the fractional release due to recoil estimated from the alpha count data* for these coated samples was 0.03 x 10⁻⁴ to 0.3 x 10⁻⁴.

To evaluate the cladding, the data in Table 1.4-4 were compared to the data obtained from test LTC-67B† (a test at the same temperature on a similar matrix but without the cladding); the fractional release was a factor of 4 to 5 less for the test with clad specimens (LTC-69). The I¹³¹ release from test LTC-69 was only a factor of 2 lower but this was probably because the traps were still affected to some degree by the transient release caused by thermal cycles.

A comparison of the data from test LTC-69 with the data obtained from test LTC-62‡ indicated that the R/B values were essentially the same. LTC-62 was a test at 1430°C

*"High-Temperature Materials Program Progress Report No. 24, Part B," GE-NMPO, GEMP-24B, June 28, 1963, p. 10.

†"High-Temperature Materials Program Progress Report No. 28, Part B," GE-NMPO, GEMP-28B, November 11, 1963, p. 20.

‡Bittel, loc. cit.

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on 6BF-116 tubes each fully clad with Y_2O_3 -stabilized ZrO_2 ; the tubes were made with regular fuel particles 4 to 5 microns in diameter. The R/B values from test LTC-62 were 2×10^{-4} for I^{131} and 3.5×10^{-5} for Kr^{89} (measured as Sr^{89}).

SUMMARY AND CONCLUSIONS

A process was developed for the rapid comminution of friable fuel compacts to powder of the proper size for spheroidization, with a minimum yield of fines.

Installation of a new plasma torch of improved design resulted in better control of the composition and properties of spheroidized fuel particles. With the new torch, UO_2 - Y_2O_3 - ZrO_2 powders were spheroidized at rates of approximately 400 grams per hour to yield a product from which less than 10 percent of the material was rejected by air elutriation and inclined plane separation.

Fuel spheres approximately 50 microns in diameter were coated uniformly with BeO or Y_2O_3 -stabilized ZrO_2 by a vapor reaction process in a spirally agitated fluidized bed. During subsequent testing, no interdiffusion between the fuel spheres and the BeO coating was observed at temperatures up to at least 1680°C . Some interdiffusion between the fuel spheres and Y_2O_3 -stabilized ZrO_2 cladding was observed at temperatures above approximately 1500°C . When the BeO-coated spheres are incorporated into a BeO matrix and sintered at 1680°C for 2 hours, the BeO coating grains show some growth into the BeO matrix.

Uncoated F-204 spheres were incorporated into a BeO matrix by extrusion and sintering. The modulus-of-rupture strength was less and the rate of fuel loss was somewhat greater for sintered tubes containing spherical fuel particles approximately 50 microns in diameter than for tubes containing impact-milled fuel powder with an average particle diameter of 4 to 5 microns. The difference in strength was reduced in later tests by the addition of a grain growth inhibitor (ZrO_2 sol) to the BeO-matrix material containing spherical fuel particles. The higher fuel loss for the fuel containing spherical particles is probably related to fuel particles at the surface of the sintered body being partially exposed, thus providing a larger reservoir of UO_2 than the finer dispersion.

Fueled tubes, either with or without Y_2O_3 -stabilized ZrO_2 cladding and all containing uncoated F-204 spheres, were subjected to irradiation testing in a flowing air atmosphere at 1230°C in the LITR. The fission product release data show a slight diffusion addition to the expected recoil release for uncoated tubes containing F-204 spheres. The presence of an Y_2O_3 -stabilized ZrO_2 cladding on the body fueled with F-204 spheres improved the fission product retention by a factor of 4 to 5.

PLANS AND RECOMMENDATIONS

Spheres of enriched F-204 are being coated with BeO and will be incorporated into a BeO matrix containing ZrO_2 sol to inhibit matrix grain growth and growth of coating grains into the matrix. The resulting fueled specimens, with and without Y_2O_3 -stabilized ZrO_2 cladding, will be subject to irradiation testing in the C-48 facility of the LITR to determine their irradiation stability and fission product retention capability. Post-irradiation strength and microstructure examination will be completed.

Since no interdiffusion between fuel spheres and BeO coating was observed up to 1680°C and since a thin layer (2 to 3 microns) of Y_2O_3 -stabilized ZrO_2 cladding should be adequate to prevent growth of BeO coating grains into a BeO matrix, F-204 spheres will be coated with BeO over which a thin layer of Y_2O_3 -stabilized ZrO_2 will be deposited. The coated spheres will be incorporated into a BeO - 2 percent ZrO_2 sol matrix to assess their stability during sintering for 2 hours in hydrogen at 1680°C .

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The oxidation of F-204 spheres (both uncoated and coated) will be studied in thermal balance experiments.

The 50-kilowatt inductively coupled plasma generator will be placed in operation and used to prepare experimental quantities of spherical F-204 fuels. Spectrographic equipment will be used to measure the temperature of the inductively coupled plasma.

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2. FUEL ELEMENTS

2.1 REFRACTORY-METAL FUEL ELEMENT MATERIALS RESEARCH (57005)

The objective of this work is to develop high-temperature refractory-metal fuel element materials and to define their time - temperature, fission product retention, and nuclear burnup capabilities for high-temperature reactor applications.

In support of this objective, continuing research evaluations were conducted in the areas of (1) fueled core development, (2) fuel element fabrication, (3) laboratory evaluations, and (4) in-pile evaluations of fuel element specimens.

The core composition used for most of this work was W - 60UO₂^{*}, although other compositions were studied. The cladding materials investigated were primarily tantalum and tantalum alloys, while niobium and W - 25Re alloy were tested to a limited extent. Laboratory tests were conducted on specimens of various fuel element systems but with the change in emphasis from short-time, maximum-temperature capabilities to long-time (1000-hour) stability in the range of 1800° to 2200°C. The in-pile experiments consisted of two tests in the LITR of Ta-clad W - 60UO₂ specimens at temperatures of 1000° to 2200°C and one test in the ETR at temperatures of 1435° to 1925°C.

FUELED CORE DEVELOPMENT

The objective of this phase of the refractory-metal fuel element research is the development of metallic - ceramic core bodies with maximum high-temperature capabilities. Previous studies[†] established that high-density cores in which the fuel particles were isolated in a continuous metallic matrix offered the maximum capabilities. This type of core structure was achieved by using an agglomerated form of UO₂, developed for this application. During the past year, the sintering procedure for W-UO₂ cores containing the agglomerated fuel was optimized to obtain maximum density with minimum fuel loss and to control the oxygen-to-uranium ratio of the UO₂ fuel particles.

In addition, W-UO₂-ThO₂ core bodies were prepared in an effort to increase high-temperature core capabilities by increasing the fuel melting point. The ability of ThO₂ to improve the high-temperature stability of UO₂ was evaluated, and the properties of W-UO₂-ThO₂ core structures were partially determined.

Preparation of W-UO₂ Cores

The preparation of W-UO₂ fueled core bodies consisted of blending tungsten powder of 2- to 5-micron particle size with agglomerated UO₂ of 150-micron particle size, cold-pressing this blend in a steel die to form cylindrical bodies, and sintering these in hydrogen at 2500°C. The details of this procedure were documented during the past year.[‡]

^{*}Core compositions are given in volume percent; cladding compositions, in weight percent.

[†]"Second Annual Report - High-Temperature Materials and Reactor Component Development Programs," GE-NMPO, GEMP-177B, February 28, 1963, pp. 163-164.

[‡]"Procedure Manual for Fabrication of Refractory Metal Fuel Element Specimens," GE-NMPO, TM 63-7-13, July 1963.

Reduction of Fuel Loss

In an effort to improve core stability, fuel loss investigations were undertaken to determine the effects of (1) sintering temperature, (2) time at constant temperature, and (3) core density on fuel loss. Measurements of W-UO₂ weight losses as a result of vaporization of UO₂ (fuel loss) from the surface were used as an indication of core stability.

Effect of Sintering Temperature on Fuel Loss - One series of W - 60UO₂ cores was sintered at 2500°C for times up to 10 hours, and a second series was sintered at 2400°C for times up to 14 hours. Weight losses under low hydrogen flow conditions, determined as a function of time (Figure 2.1-1), indicated the overall fuel loss rate at 2500°C is about double the rate at 2400°C. The fuel loss after 1 hour at 2400°C was approximately 11 mg/cm² compared to 40 mg/cm² at 2500°C. This loss represented a partial depletion of the UO₂ particles located at the surface of the core specimen shown in the photomicrographs of Figure 2.1-1. The layer depleted of UO₂ measured about 0.035 millimeter in depth after 4 hours at 2400°C and 0.305 millimeter in depth after 4 hours at 2500°C. Although this fuel-depleted layer created no problem when the core was clad, since it was subsequently removed by centerless grinding, the relatively high fuel loss rates during sintering emphasized the need for optimizing core structure and sintering procedures.

Fig. 2.1-1 - Fuel loss as a function of time for W-60UO₂ core specimens sintered at 2400°C and 2500°C in hydrogen

Another series of two groups of W - 60UO₂ cores was sintered for 18 hours at 2000°C and 2200°C in hydrogen. At both temperatures, 95 to 96 percent of theoretical density was attained, and the fuel losses averaged 38 mg/cm² at 2000°C and 43 mg/cm² at 2200°C.

Effect of Time at Constant Temperature on Fuel Loss - To determine the time - temperature effects on fuel loss, W-UO₂ core specimens, initially hydrogen-sintered at 2500°C for 1 hour, were centerless-ground to present a fresh fueled surface and then heated in three groups for 16 hours each at 2000°, 2200°, and 2400°C in hydrogen. Fuel losses, shown in Figure 2.1-2 as a function of temperature, were somewhat lower than for the cores sintered at 2000°C and 2200°C.

Fig. 2.1-2 - Fuel loss versus temperature for W-60UO₂ core specimens treated for 16 hours in hydrogen

Effect of Density on Fuel Loss - The effect of lower fuel loadings on the sintered density and fuel losses of W-UO₂ cores was also investigated. Core specimens containing 40, 50, and 60 volume percent agglomerated UO₂ in a tungsten matrix were sintered at 2500°C for 1 hour in hydrogen and then subjected to a stability test at 2600°C for 1 hour in hydrogen. The results, shown in Table 2.1-1, indicate that similar high densities were attained for all cores, but the fuel losses increased with increased fuel loading.

In addition, to increase core density and possibly reduce fuel losses, the effects of isostatic pressing of the green cores were investigated. Four specimens each of W - 40UO₂ and W - 60UO₂ were initially pressed in a steel die to establish the cylindrical geometry and then were isostatically pressed at 4900 kg/cm² which is more than double the pressure normally used in die pressing. These compacts were sintered at 2500°C for 1 hour in hydrogen. The results are shown in Table 2.1-2 with comparative data for W - 60UO₂ cores cold-pressed in a steel die at 2100 kg/cm². Isostatically pressed compacts sintered to higher densities than the die-pressed compacts, but the weight losses did not differ appreciably.

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TABLE 2.1-1
EFFECT OF FUEL LOADING ON SINTERED DENSITY AND FUEL LOSSES
FOR W- UO_2 CORE SPECIMENS AT 2500°C AND 2600°C

Core Composition, vol %	After Sintering At 2500°C For 1 Hr In H_2^a		Fuel Loss After A Stability Test At 2600°C For 1 Hr In H_2 , mg/cm ²
	Density, percent of theoretical	Fuel Loss, mg/cm ²	
W - 60 UO_2	95	66	185
W - 50 UO_2	95	62	130
W - 40 UO_2	94	49	44

^aEach value represents an average of four core specimens prepared from one blend.

TABLE 2.1-2
EFFECTS OF ISOSTATIC PRESSING
ON SINTERED DENSITY OF W- UO_2 CORE SPECIMENS

Core Composition, vol %	Cold-Pressing Method	Sintered At 2500°C For 1 Hr In H_2^a	
		Density, percent of theoretical	Weight Loss, %
W - 40 UO_2	Isostatic ^b	94	1.0
W - 60 UO_2	Isostatic ^b	94	1.8
W - 60 UO_2	Die ^c	92	2.0

^aValues shown represent average of four specimens.

^bInitially pressed in steel die at 1265 kg/cm² and then sealed in rubber and isostatically pressed at 4900 kg/cm².

^cCold-pressed in 15.9-millimeter diameter steel die at 2100 kg/cm².

In the determination of physical and mechanical properties of the W - 60 UO_2 core at high temperature, the loss of UO_2 during testing must be limited to prevent changes in characteristics or composition of the specimen. Fuel losses were restricted by packing the sintered W - 60 UO_2 specimen in high-fired UO_2 granules in a tungsten crucible. The packed specimen was heated at 2600°C for 4 hours in helium which increased the density from 95 to 97 percent of theoretical with no measurable fuel loss. These results show that fuel loss from a W- UO_2 core is not a significant problem at temperatures up to 2600°C if the core is adequately contained or clad and, further, that physical properties measurements can be made without suffering compositional changes if the core can be packed in UO_2 .

Preparation of W- UO_2 - ThO_2 Cores

Use of ThO_2 in the W- UO_2 fueled core increases the high-temperature (2800°C) core capabilities by increasing the melting point of fuel. More recently, ThO_2 was found effective in reducing the reactivity of fuel with the tantalum cladding at 2200°C.

The high-temperature stability of thoriated UO_2 was demonstrated by preparing core specimens of W - 48 UO_2 - 12 ThO_2 and sintering at 2600°C for 1 hour in hydrogen to 94 percent of theoretical density. These unclad cores were then tested either at 2800°C for 1 hour in hydrogen or at 2900°C for 5 minutes in helium. Visual and metallographic examination of these specimens revealed no evidence of fuel melting, as shown in the photomicrograph of Figure 2.1-3.

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Neg. 1942

250 X

Fig. 2.1-3—Photomicrograph of W-48UO₂-12ThO₂ core specimen after heating at 2900°C in helium for 5 minutes

Melting Point of UO₂-ThO₂ - To verify the melting point of UO₂-ThO₂ mixtures, specimens of UO₂ blended with 10, 20, and 30 weight percent ThO₂ were sintered at 2400°C for 2 hours in hydrogen to densities of 91, 85, and 80 percent of theoretical, respectively. The specimens were sealed in W - 25Re alloy cans to prevent vaporization and allow accurate temperature measurements. Initially, the specimens were heated at 2900°C for 15 minutes; when the cans were opened, no evidence of melting was observed for any of the 3 compositions. Another canned specimen of UO₂ - 10ThO₂ completely melted when heated to 2950°C. These data located the melting point of the UO₂ - 10ThO₂ composition between 2900° and 2950°C. The 20 and 30 percent compositions showed no evidence of melting at 2950°C. Determination of exact melting points was not possible at these extremely high temperatures.

Reduction of Fuel Losses by ThO₂ Additions - As previously shown in the studies of sintering temperature effects, the loss of UO₂ by vaporization from W - 60UO₂ during sintering at 2400°C in hydrogen amounted to approximately 11 mg/cm²-hr. The addition of 10 weight percent ThO₂ to the UO₂ resulted in a reduction of the fuel loss rate, over a period of 14 hours at 2400°C, to about 4 mg/cm²-hr. This limited fuel loss was verified by metallographic examination which revealed that the fuel was not completely vaporized in the depletion zone and that the maximum depth of depletion was 0.36 millimeter compared to a depth of 0.51 millimeter for W - 60UO₂ tested under the same conditions. The further improvements in the core stability effected by ThO₂ additions are discussed in "Laboratory Evaluations" of Ta-clad specimens.

Physical Properties of W-UO₂ Core Material

Thermal Expansion Properties - Thermal expansion measurements were made for various W-UO₂ core compositions using rod specimens, 6.35 millimeters in diameter by 5.85 centimeters in length, prepared by the same procedure as the standard fueled cores. At least two runs of about 8 hours each were made for each specimen. The standard practice

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was to use a helium atmosphere in the furnace to prevent fuel composition changes that might occur in high-temperature hydrogen. Thermal expansion characteristics were determined at temperatures up to 2200°C for W-UO₂ specimens containing 40, 50, and 60 volume percent UO₂ and for W - 48UO₂ - 12ThO₂ specimens. The results of these measurements are compared with previous values for UO₂ in Figure 2.1-4.

Fig. 2.1-4 - Linear thermal expansion of various W-UO₂ core compositions compared with UO₂

Specimens of the W - 60UO₂ composition containing both as-received and agglomerated UO₂ were tested; UO₂ particle size had no significant effect on thermal expansion characteristics. The addition of ThO₂ slightly decreases the thermal expansion of the standard W - 60UO₂. The expansion of W - 40UO₂ closely matches that of tantalum and the W - 25Re alloy.

In addition, the thermal expansion of cladding materials was measured at temperatures up to 2500°C using sheet specimens of Mo, Re, and W - 25Re. The results for these various materials are shown in Figure 2.1-5.

Thermal Conductivity - The thermal conductivity of the W - 60UO₂ composition containing agglomerated fuel was determined in the temperature range from 1100° to 2250°C and of UO₂ in the range from 1000° to 2540°C. The specimens were 5.08 centimeters in diameter and 1.27 centimeters thick with an axial hole to accommodate an internal heating element. Seven discs were stacked vertically in a tungsten resistance furnace, and the radial temperature gradients corresponding to given imposed heat flux values were measured. The W - 60UO₂ specimens had an average density of 95 percent of theoretical, while the UO₂ specimens were sintered to 96 percent of theoretical density and had an oxygen-to-uranium ratio of 2.00 (± 0.01).

The data obtained for the two materials are shown in Figure 2.1-6. The values for W - 60UO₂ range from 0.27 watt/cm-°C at 1100°C to 0.21 at 2250°C. These values are within 10 percent of values calculated from published data for tungsten and UO₂. The data for

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Fig. 2.1-5—Linear thermal expansion properties of W-25Re, Re, and Mo compared to W-UO₂ core

Fig. 2.1-6—Thermal conductivity versus mean temperature for W-60UO₂ and UO₂

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UO₂ should be considered as preliminary since the scatter at the higher temperatures was about ± 20 percent. A new set of specimens was prepared and will be tested using refined techniques. From the present data, the thermal conductivity of UO₂ at 2500°C appears to be approximately 0.06 watt/cm-°C.

Enthalpy - Enthalpy data at temperatures up to 2200°C were obtained for W - 60UO₂ specimens containing agglomerated fuel and sintered to 95 percent of theoretical density. For these determinations the specimens were enclosed in an evacuated capsule of molybdenum, 1.58 centimeters in diameter by 3.8 centimeters in length. The capsule was heated to temperature in argon and dropped into an adiabatic calorimeter to measure the enthalpy.

The resulting data for W - 60UO₂ are shown in Figure 2.1-7 in comparison with UO₂ data determined in the same manner and tungsten data reported elsewhere.* The measured enthalpy values of W - 60UO₂ are approximately 6 percent below the values calculated from tungsten and UO₂ data.

Fig. 2.1-7 - Enthalpy of W-60UO₂ compared to UO₂ and tungsten

Stress-Rupture Properties - Stress-rupture test facilities were constructed and checked for reliability by operating at temperatures up to 2750°C using refractory-metal specimens in hydrogen or helium atmospheres. Button-head specimens, 6.35 centimeters in length with a gage length of 2.54 centimeter, were machined from rods of W - 60UO₂ sintered to a density of 94 to 97 percent of theoretical. One group of specimens was tested in hydrogen at 2260°C with heating and cooling in vacuum or argon. A second group was tested in helium. The results of these tests are shown in Table 2.1-3 and Figure 2.1-8. The results for tungsten rod specimens are shown for comparison. These data indicate a 1-hour rupture strength for W - 60UO₂ of about 83 kg/cm² at 2260°C in helium.

Also shown in Table 2.1-3 are the densities of the specimens before and after testing. All specimens were sintered at 2500°C for 1 hour in hydrogen prior to machining and were

*M. Hoch and H. L. Johnston, "A High Temperature Drop Calorimeter—Heat Capacities of Ta and W Between 1000° and 3000°K," *Journal of Physical Chemistry*, Vol. 65, No. 885, 1961, p.1184.

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TABLE 2.1-3
STRESS-RUPTURE AND CREEP DATA
FOR W - 60UO₂ TESTED IN HYDROGEN OR HELIUM AT 2260°C

Test Atmosphere	Stress, kg/cm ²	Rupture Time, hr	Elongation, %	Linear Creep Rate, 10 ⁻⁴ min ⁻¹	Density, percent of theoretical	
					As-Machined	Post-Test
Hydrogen	21.09	3.80	5.2	1.7	94.0	87.3
	21.09	5.46	4.8	1.3	96.3	80.1
	42.18	0.95	4.7	5.8	95.2	92.3
	70.30	0.46	4.6	2.5	94.4	87.6
	70.30	0.60	4.2	1.5	96.0	91.3
Helium	21.09	10.0	4.2	0.29	96.8	81.5
	21.09	12.39	5.4	0.29	95.4	77.2
	52.73	2.1	7.9	2.5	97.6	90.9
	70.30	1.23	5.8	3.6	96.2	94.0
	70.30	1.45	10.4	3.6	96.5	93.8

Fig. 2.1-8 - Stress-rupture properties of sintered W-60UO₂ tested in hydrogen and helium at 2260°C compared with wrought tungsten rod

tested in the as-machined condition. Based on a water immersion method of measurement, densities averaged 96 percent of theoretical. After testing in hydrogen or helium, the density of the gage sections ranged from 77 to 94 percent of theoretical depending on the time at temperature. Metallographic study of the structure revealed that the UO₂ had vaporized from the surface of the gage section to depths ranging from 0.147 to 0.465 millimeter after 5.4 hours in hydrogen and to a somewhat lesser depth in helium. These results suggest that stress-rupture tests of W-UO₂ should be conducted at lower temperatures or the specimens should be clad to prevent the fuel losses and density variations.

Electrical Resistivity - The electrical resistivity of the W - 60UO₂ core composition was determined in the temperature range of 800° to 2200°C by using a four-probe Kelvin Bridge technique. The rod specimen was made with -100/+200 mesh agglomerated UO₂. After isostatic pressing at 5000 kg/cm², the compact was sintered at 2500°C in hydrogen

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for 1 hour to 94 percent of theoretical density. The rod was centerless-ground to a diameter of 6.35 millimeters.

The resistivity versus temperature data were obtained using this specimen for three runs. The specimen was heated in a tungsten resistance furnace with a helium flow of 140 liters per hour. Consistent values were obtained on heating and cooling cycles and data for second and third runs were in close agreement, as shown in Figure 2.1-9. The same unit of measurement change should be noted on the ordinate of Figure 2.1-9:

Fig. 2.1-9 - Electrical resistivity of W-60UO₂ as a function of temperature

CLAD FUELED SPECIMEN FABRICATION

The procedures for the fabrication of Ta-clad W-UO₂ fueled specimens were established early in this research effort. The work of the past year on this phase consisted of improvements and refinements of techniques and establishment of specifications for high-quality tubing used as cladding on the specimens. A procedure manual* was prepared which describes in detail the steps required for fabrication of refractory-metal fuel element specimens. Although the procedure was revised as the technology improved, the method in brief consisted of the following steps:

1. Machining the sintered W-UO₂ cores to fit the tantalum tubing
2. Cleaning the cores of volatiles (machining oil residues) by heating to 2200°C in hydrogen
3. Cleaning the tantalum cladding components by heating to 1000°C in high vacuum
4. Assembling the cladding over the core and sealing by electron-beam welding
5. Inspecting for helium leaks by mass spectrometry
6. Bonding the cladding to the core by pressurizing to 700 kg/cm² in helium at 1650°C
7. Inspecting for bonding and gas leaks
8. Proof-testing for 2 hours at 2200°C in helium

*"Procedure Manual for Fabrication of Refractory Metal Fuel Element Specimens," GE-NMPO, TM 63-7-13, July 1963.

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Most of the specimens fabricated for laboratory stability tests were simple cylindrical specimens 1.27 centimeters in diameter and 1.9 centimeters in length. The cladding thickness was nominally 0.5 millimeter except the end plates which, during the past year, were increased to a minimum of 1.5 millimeters to prevent the heat of electron-beam welding from penetrating to the fueled core. Specimens fabricated for in-pile experiments were also 1.27 centimeters in diameter, but were 3.8 centimeters in length and had an axial center tube with a 3.2-millimeter bore.

During the preparation of the various specimens, numerous defects were encountered in the tubular cladding stock and, to a lesser extent, in the sheet stock procured from commercial sources. The faults were not only mechanical defects, but chemical and physical instability was noted when the specimens were heated to elevated temperatures. The results of chemical and metallographic analyses are shown in Table 2.1-4.

TABLE 2.1-4
QUALITY CONTROL DATA ON CLADDING COMPONENTS

Material ^a	Product	Grade ^b	As-Received Composition, ppm							High-Temperature Stability Test In H ₂			
			O ₂	N ₂	C	Fe	Ni	Al	Si	Temperature, °C	Time, hr	Evaluation	
Nb	0.016 inch sheet	PM	295	120	355	-	-	-	-	2400	100	Significant	Small
	0.5 inch OD tube	PM	430	185	150	135	130	20	60	2400	100	Significant	Small
Mo - 50Re	0.020 inch sheet	PM	45	10	40	25	< 1	7	< 1	2400	100	Slight	Medium
Mo	0.020 inch sheet	AC	75	12	210	-	-	-	-	2400	100	Nil	Large
	0.5 inch OD tube	PM	95	20	150	<100	<100	<100	<100	2400	100	Excessive	Small
Ta	0.020 inch sheet	AC	95	60	50	-	-	-	-	2600	10	Nil	Large
	0.5 inch OD tube	PM	130	20	75	145	20	20	25	2600	10	Significant	Small
Ta - 10W	0.020 inch sheet	AC	40	10	35	12	-	-	-	2600	10	Nil	Large
W - 25Re	0.020 inch sheet	PM	40	8	40	25	10	10	3	2800	10	Slight	Small

^aAlloy compositions are weight percent.

^bPM indicates powder metallurgy product; AC indicates arc-cast materials.

Comparative microstructures of arc-cast and powder metallurgy tantalum are shown in Figure 2.1-10 in the as-received condition and after treatment at 2600°C for 10 hours in hydrogen. Essentially no difference in microstructure of the two materials was apparent in the as-received condition. However, the powder metallurgy tantalum showed excessive porosity after the 2600°C treatment while the arc-cast tantalum showed no porosity but the grains had grown so much that the sheet was single grain in thickness (0.38 mm). Ten-hour tests of Ta-clad W-UO₂ specimens at 2500°C and 2600°C showed the excessive porosity in the powder metallurgy tantalum but it did not increase the core - cladding reactivity. Therefore, most of the test specimens fabricated were clad with powder metallurgy tantalum to avoid the large-grained condition of arc-cast material and the attendant tendency to leak through the grain boundaries.

Many types of mechanical defects were found in tubular cladding stock procured from commercial sources. For the most part, the defects were observed in cold-finished tantalum and Ta - 10W alloy tubing and appeared to be a result of commercial fabrication practices which are not adequate to produce tube material for use as fuel element materials.* Photomicrographs of typical defects are shown in Figure 2.1-11.

Nondestructive test equipment employing eddy-current techniques was developed at GE-NMPO to detect defects in tubing to as low as 5 percent of the wall thickness.† Ultrasonic inspection equipment is also being used for the detection of axial and longitudinal defects

*"High-Temperature Materials Program Progress Report No. 29, Part B," GE-NMPO, GEMP-29B, December 6, 1963, pp. 44-45.

†A. W. Bauer, "Invention Disclosure for a Multiple Frequency Eddy Current Tubing Tester," GE-NMPO, TM 63-12-11, December 1963.

Neg. 1963

ETCHED
AS-RECEIVED

100 X

Neg. 1964

ETCHED
TREATED AT 2600°C

100 X

POWDER METALLURGY TUBING

Neg. 1961

ETCHED
AS-RECEIVED

100 X

Neg. 1962

ETCHED
TREATED AT 2600°C

100 X

ARC-CAST SHEET

Fig. 2.1-10—Comparative microstructures of arc-cast and powder metallurgy tantalum cladding materials before and after treatment at 2600°C for 10 hours in hydrogen.

Neg. 3451

100 X

LONGITUDINAL SECTION OF LAMINATION ON
INSIDE SURFACE OF 6.35-MM OUTSIDE DI-
AMETER BY 0.51-MM WALL TUBING

Neg. 3668

250 X

TRANSVERSE SECTION SHOWING RADIAL
CRACK ON INSIDE SURFACE OF 1.75-MM
OUTSIDE DIAMETER BY 0.20-MM WALL TUBING

Fig. 2.1-11 - Photomicrographs of arc-cast tantalum tubing of two sizes
showing typical defects in tubing walls

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and laminations. By showing the various tubing fabricators that this sensitive equipment could be applied to their products, the quality of recent orders for tantalum tubing was improved. Preliminary specifications regarding defects and inspection procedures were compiled and applied to all new orders for refractory-metal tubing, with the exception of W - 25Re alloy tubing which is still produced on a best effort basis.

One lot of W - 25Re tubing was evaluated for metallographic structure and ductility. Approximately 3 meters of each of two sizes were received. The nominal 1.65-millimeter-diameter tubing varied from 1.57 to 1.70 millimeters, and the nominal 1.40-millimeter-diameter tubing varied from 1.27 to 1.42 millimeters. Wall thickness varied from 0.20 to 0.28 millimeter. No gross porosity nor cracks were found by pressure testing. The as-received (stress-relieved) tubing was so ductile that 90-degree bends on a 3-millimeter radius were made before longitudinal splitting occurred. After heating at 2800°C for 1 hour in hydrogen, the recrystallized structure was brittle. Specimens of tubing of each size were treated in vacuum (4×10^{-5} Torr) at 2300°C in an effort to reduce the interstitial content of the W-Re alloy, but no improvement in ductility was achieved. Metallographic examination of this tubing revealed that the quality was about the same as material previously evaluated and that considerable development of processing techniques will be necessary before W-Re tubing of fuel element quality becomes available commercially.

Specimen Fabrication for High-Burnup Experiment

An in-pile experiment was designed to yield high-burnup data for the Ta-clad W - 60UO₂ system. This required a specimen having a relatively thin fueled section for uniform burnup. The specimen configuration is shown in Figure 2.1-12. The W - 60UO₂ core was prepared by standard sintering procedures, but the tube-like core with a wall thickness of 0.68 millimeter required machining to extremely close tolerances. The tantalum cladding components were also machined to close tolerances so that when the specimen was gas-pressure-bonded, the inner and outer tubes would be metallurgically bonded with the end plugs and tungsten core matrix. Figure 2.1-13 shows that complete metallurgical bonding was achieved between all specimen components by this process. After ultrasonic inspection to check the bonds, the two major outside diameters were ground to a tolerance of ± 0.0064 millimeter, and the concentricity was maintained within ± 0.013 millimeter. Six specimens containing enriched UO₂ were prepared for the 33MT115 experiment, and the best four were selected for assembly in the cartridge. All of the tantalum cladding components were fabricated of arc-cast tantalum tubing. The fueled cores which were sintered at 2500°C had a final density after machining of 94 percent of theoretical. The results of the testing of these specimens in the ETR are discussed in a subsequent section on "In-Pile Evaluations."

Fig. 2.1-12 - Configuration of Ta-clad W-60UO₂ fuel element specimen for high burnup experiment 33MT115

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Fig. 2.1-13—Longitudinal section of autoclaved Ta-clad W-UO₂ fuel element specimen of 33MT115 design showing excellent bonding of all components

Specimen Fabrication for LITR Experiments

The Ta-clad W - 60UO₂ specimens used for the experiments in the LITR were 1.27 centimeters in diameter by 3.81 centimeters in length with a single axial hole 3.17 millimeters in diameter. The tantalum cladding was nominally 0.51 millimeter in thickness and was derived from powder metallurgy material. One such specimen was tested in the LTFF-5 experiment at temperatures as high as 2200°C with only minor release of fission products. The preparation of a specimen for LTFF-6 was the same as that of LTFF-5 except a proof-test of 2 hours at 2200°C in helium was imposed on the finished specimen before assembly into the cartridge. As a result of this proof-test, it was discovered that small leaks developed in the Ta cladding during gas-pressure-bonding or the 2-hour proof-testing. The leaks in the tantalum cladding were detected by pressurizing the specimens in helium at 3.5 to 19.2 kg/cm² for 15 minutes and then inspecting for gas evolution while immersed in methanol, or by means of a mass spectrometer. The leaks which developed during gas-pressure-bonding were identified as cracks or pin holes in the weld area or center tube of the specimens. The leaks which developed during proof-testing were of a different nature, however, and seemingly developed in the grain boundaries of the tantalum cladding. As a result, an extensive study was initiated to explain and resolve this new leaking problem and to identify cladding materials which are not susceptible to grain boundary weakening

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upon recrystallization. The findings of this study are discussed in the following section, "Laboratory Evaluations."

Since efforts to prepare a leak-free specimen for the LTFF-6 experiment were fruitless, the best specimen of the rejected group of 14 was selected. No leaks were detected in this specimen by the methanol test, but a slight leak was detected by the mass spectrometer test. The specimen was used despite the leak, since useful fission gas release data could be obtained from a specimen with a known leak and the materials stability information would be equally useful. The operation of this in-pile experiment is described in "In-Pile Evaluations."

LABORATORY EVALUATIONS

Laboratory evaluations were used to determine the maximum time - temperature capabilities of the various fuel element systems. Although several specimen designs were used, the most common was a solid right cylinder, 1.27 centimeters in diameter by 1.91 centimeters in length. The majority of these specimens were tested in tungsten resistance furnaces at temperatures ranging from 1930⁰ to 2900⁰C in either hydrogen or helium for times varying from 1 to 1100 hours. Thermocouples of W / W - 26Re were used to measure temperatures up to 2000⁰C; the higher test temperatures were measured with optical pyrometers. The evaluation of these specimens included visual examination for gross or obvious external defects, mass spectrometer leak-check, ultrasonic bond check, and both metallographic and electron microprobe analysis for core - cladding reactivity.

Specimens of five fuel element systems were evaluated during the past year. The majority of these specimens were clad with tantalum, although claddings of niobium, molybdenum, and W - 25Re alloy were also evaluated. About mid-year, the problem of gas leaks in the standard Ta-clad W - 60UO₂ specimens was encountered after proof-testing at 2000⁰C. Laboratory evaluations of the Ta system were then divided into two primary efforts: (1) development of the Ta-clad W-UO₂-ThO₂ system and (2) investigation of the problem of leaks in the Ta-clad W-UO₂ specimens. Laboratory tests were made on Mo-clad W-UO₂, W-Re-clad W-UO₂-ThO₂, Nb-clad Mo-UO₂, Ta-clad W-UO₂-ThO₂, and Ta-clad W-UO₂ systems. The processing data and test results on specimens of the first four systems are summarized in Table 2. 1-5, while the data on the Ta-clad W-UO₂ specimens are described later.

Mo-Clad W-UO₂ System

Molybdenum is difficult to obtain in the form of high-quality, thin-wall tubing. Also, because of its inherent brittleness, molybdenum is difficult to process. It is compatible with UO₂, however, and the results obtained on Mo-clad W - 60UO₂ specimens indicated good time - temperature capabilities. The first specimen of this system (designated No. 76 in Table 2. 1-5) to contain agglomerated fuel was tested at 2400⁰C for 100 hours in hydrogen. As previously reported,* the cladding shell used on this specimen was inferior quality tubing which showed gross deterioration in the form of blisters and porosity, yet no evidence of fuel penetration was detected. As shown in Figure 2. 1-14, the higher quality molybdenum sheet used as end plates experienced only moderate core - cladding reactivity during this test. The specimen was not checked for gas leaks but, since metallographic examinations of both a transverse and a longitudinal section revealed no gross fuel loss from the core, the specimen could not have had cladding leaks.

W-Re-Clad W-UO₂-ThO₂ System

The W - 25Re alloy offers excellent high-temperature capability as a cladding for refractory-metal fuel elements. Two W - 25Re-clad W-UO₂-ThO₂ specimens were tested;

*"High-Temperature Materials Program Progress Report No. 23, Part B," GE-NMPO, GEMP-23B, May 31, 1963, p. 16.

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TABLE 2. 1-5

PROCESSING DATA AND TEST RESULTS ON REFRACTORY-METAL FUEL ELEMENTS^a

Specimen	System		Core Sintering Temperature, °C	Core Density, percent of theoretical	Bench-Test Conditions			Post-Test Inspection Results			Core - Cladding Reactivity
	Cladding	Core Composition, vol %			Temperature, °C	Time, hr	Atmosphere	Visual Condition	Bond Check	Leak Check	
76	Mo	W - 60UO ₂	2400	97	2400	100	H ₂	Minor blistering of cladding shell	Only blisters not bonded	-	Moderate
73	W - 25Re	W - 48UO ₂ - 12ThO ₂	2500	95	2800	10	H ₂	No defects	Bonded	No leaks	None
78	W - 25Re	W - 48UO ₂ - 12ThO ₂	2500	95	2900	1	H ₂	No defects	Bonded	No leaks	None
70	Nb	W - 60UO ₂	2400	98	2200	100	H ₂	End plates bulged	Shell bonded	-	Moderate
84	Nb	W - 60UO ₂	2400	95	2200	100	H ₂	Minor blistering of cladding shell	Only blisters not bonded	Several	Moderate
86	Nb	Mo - 50UO ₂	2400	93	2200	100	H ₂	Minor blistering of cladding shell	Only blisters not bonded	-	Moderate
100	Nb	Mo - 50UO ₂	2400	94	1800	1019	He ^b	Minor blistering of cladding shell	Only blisters not bonded	No leaks	Test continuing
129	Nb	Mo - 50UO ₂	2400	94	1800	1019	He ^b	No defects	Bonded	No leaks	Test continuing
133	Nb	Mo - 50UO ₂	2400	94	1800	1019	He ^b	No defects	Bonded	No leaks	Test continuing
143	Nb	Mo - 50UO ₂	2400	94	1800	1019	He ^b	No defects	Bonded	No leaks	Test continuing
74	Ta	W - 48UO ₂ - 12ThO ₂	2600	90	2700	10	H ₂	No defects	Bonded	Several	Gross
110	Ta	W - 48UO ₂ - 12ThO ₂	2600	93	2600	10	H ₂	No defects	Bonded	Several	Moderate
123	Ta	W - 54UO ₂ - 6ThO ₂	2600	92	2200	117	H ₂	No defects	Bonded	No leaks	-
					2200	170	He ^b	No defects	Bonded	No leaks	-
					2200	150	He ^b	Longitudinal cracks at both ends	Bonded	Two leaks in cracks	Moderate
131	Ta	W - 60UO ₂ - 3ThO ₂ ^d	2500	89	2200	8	H ₂	No defects	Bonded	No leaks	-
132	Ta	W - 54UO ₂ - 9ThO ₂ ^d	2500	92	2200	190	Ar	No defects	Bonded	No leaks	-
					2200	115	Ar	Longitudinal crack indications	Bonded	Two leaks near ends	Moderate
140	Ta	W - 54UO ₂ - 6ThO ₂	2500	93	2200	1278	He ^b	No defects	Bonded	No leaks	Test continuing
144	Ta	W - 54UO ₂ - 6ThO ₂	2500	93	2200	767	He ^b	No defects	Bonded	No leaks	-
					2200	160	He ^b	Grain boundary separation	Bonded	One leak	Moderate
154E ^c	Ta	W - 54UO ₂ - 6ThO ₂	2500	94	2200	172	He	No defects	Bonded	No leaks	Test continuing
157E	Ta	W - 54UO ₂ - 6ThO ₂	2500	94							
159E	Ta	W - 54UO ₂ - 6ThO ₂	2500	94							
161E	Ta	W - 54UO ₂ - 6ThO ₂	2500	94							

^aAll cores sintered for 1 hour in hydrogen.^bTest conducted in static atmosphere.^cEnriched specimens containing UO₂ of 34.5 percent enrichment.^d3 volume percent ThO₂ present in the tungsten matrix.

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Fig. 2.1-14—Interface of Mo-clad W-60UO₂ specimen showing core-cladding reactivity after testing at 2400°C for 100 hours in hydrogen

one (No. 73) was tested at 2800°C for 10 hours in hydrogen, and the other (No. 78) at 2900°C for 1 hour in hydrogen. Neither showed any external or internal defects and no core-cladding reactivity. The absence of significant reactivity at 2900°C is shown in Figure 2.1-15. The fuel deposit in the grain boundaries shown in this photomicrograph occurred in several areas and penetrated the cladding to a maximum depth of 0.10 millimeter. No such fuel deposits were detected in the cladding of the 2800°C test specimen.

The W-Re-clad specimens evaluated to date were clad with commercial sheet. Shells were roll-formed from 0.51-millimeter-thick sheet and electron-beam welded. Efforts were made to fabricate W-Re-clad specimens for in-pile testing, but the inferior quality of the available tubing prevented the successful fabrication of any leak-free specimens.

Nb-Clad Mo-UO₂ System

Of the Nb-clad specimens shown in Table 2.1-5, two contained W-60UO₂ cores and five contained Mo-50UO₂ cores. The Mo-UO₂ core was selected for use with the niobium cladding because it provided a better match in thermal expansion characteristics than the W-UO₂ core. One specimen of each type was tested at 2200°C for 100 hours in hydrogen with similar results. The powder metallurgy niobium cladding on both specimens developed minor blistering. However, the end plates remained bonded and showed moderate core-cladding reactivity as shown in Figure 2.1-16.

The reaction zone on the specimen containing the Mo-UO₂ core penetrated approximately 0.10 millimeter into the niobium cladding. The void network at the outer edge of the re-

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Neg. 3146

100 X

Fig. 2.1-15 - Photomicrograph of transverse section of W-Re-clad W-UO₂-ThO₂ specimen showing excellent stability after testing at 2900°C for 1 hour in hydrogen

action zone served as the separation interface for the blisters on both specimens. Electron microprobe analyses revealed that interdiffusion of core and cladding occurred in both specimens. The Nb-clad Mo-UO₂ specimen had uranium in the niobium cladding, niobium in the molybdenum core matrix, and up to 10 percent molybdenum at the outer edge of the niobium cladding. The niobium cladding over the W-UO₂ core had both uranium and tungsten diffusion approximately halfway through the cladding in the amount of about 1 percent of the niobium cladding.

Subsequently, Nb-clad Mo-UO₂ specimens were tested at 1800°C in helium. Over 1000 hours of test time was achieved successfully at this reduced test temperature. As shown in Table 2.1-5, four specimens were continuing on test after 1019 hours. One specimen (No. 100) developed minor blistering of the cladding after 116 hours but remained leak-free. The as-tested condition of the other specimens (No. 129, 133, and 143) is shown in Figure 2.1-17. End plates, 1.57 millimeters thick, were used on these specimens, which minimized heating of the core during welding.

Ta-Clad W-UO₂-ThO₂ System

Initially, ThO₂ was added to UO₂ to achieve a fuel with a high melting point for use with W-Re-clad W-UO₂ fuel elements, as discussed previously. Thoria additions also proved beneficial in reducing the core - cladding reactivity in Ta-clad W-UO₂ specimens. Specimens containing W - 48UO₂ - 12ThO₂ cores (Nos. 74 and 110) showed definite reductions

Neg. 3188

Nb-CLAD Mo-50UO₂

100 X

Neg. 3187

Nb-CLAD W-60UO₂

100 X

Fig. 2.1-16—Microstructures of core-cladding interface sections of Nb-clad Mo-UO₂ and Nb-clad W-UO₂ specimens tested at 2200°C for 100 hours in hydrogen

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Fig. 2.1-17—Specimens of Nb-clad Mo-50UO₂ after testing at 1800°C in helium for 1019 hours including 8 thermal cycles (Neg. P64-1-8A)

in reactivity after testing for 10 hours at 2600°C or 2700°C. As shown in Table 2.1-5, these specimens remained bonded and developed no external defects. Although both specimens developed gas leaks and gross core - cladding reactivity occurred in the specimen tested at 2700°C, no significant fuel depletion from the core was detected.

In subsequent evaluations of Ta-clad W-UO₂-ThO₂ specimens, thorium additions significantly delayed the formation of gas leaks at 2200°C. The first specimen (No. 123) was tested for 117 hours in hydrogen and 170 hours in helium with no leaks or external defects. During an additional test of 150 hours in helium, longitudinal cracks developed in the weld area at both ends and leaks were detected in two of these cracks. The next two specimens (Nos. 131 and 132) were each tested for 313 hours before any leaks developed. Specimen Nos. 140 and 144 were tested for 767 hours at 2200°C in static helium with no leaks nor visual defects. Specimen No. 144 developed a single grain boundary leak during an additional 160 hours of testing. Specimen No. 140 completed 1278 hours in 13 cycles with no leaks and is continuing on test. The condition of this specimen after 1278 hours is shown in Figure 2.1-18. Although the cladding was arc-cast tantalum, it showed moderate grain growth. The surface showed significant thermal etching but only moderate grain boundary relief.

Metallographic examination of specimen No. 144 revealed very little core - cladding reactivity. The reaction zone at the interface generally involved about 0.076 millimeter of the cladding but in several areas there appeared to be an enlarged grain boundary void extending farther into the cladding. An example of this condition is shown in Figure 2.1-19. This partial penetration of the cladding was typical of the cladding leaks revealed in previous investigations.*

In view of the encouraging results obtained on this fuel element system, a group of enriched Ta-clad W - 54UO₂ - 6ThO₂ specimens was prepared for a laboratory evaluation prior to in-pile testing. Of the eight specimens fabricated, one leaked after the 2-hour proof-test at 2200°C, and four were continuing on test after successfully completing 172 hours at 2200°C in helium. The alpha count on the latter specimens was essentially nil.

*"High-Temperature Materials Program Progress Report No. 31, Part B," GE-NMPO, GEMP-31B, January 24, 1964, p. 31.

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Fig. 2.1-18—Specimen No. 140 of Ta-clad W-UO₂-ThO₂ after testing for 1270 hours at 2200°C in helium (Neg. P64 1 25)

Neg. 3888

100 X

Fig. 2.1-19—Photomicrograph of core-cladding interface of specimen No. 144, Ta-clad W-UO₂-ThO₂, which developed a grain boundary leak after testing for 927 hours at 2200°C in helium

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In view of these results, the preparation of an in-pile specimen (LTFF-7) of this fuel element system was begun.

Ta-Clad W-UO₂ System

More than half the specimens subjected to laboratory stability tests during the year were of the Ta-clad W-UO₂ system. The processing data and test results for the more significant specimens are summarized in Table 2. 1-6. Several specimens were tested at 2600°C for 10 hours in a continuation of the CY-62 testing program for determining high-temperature, short-time capabilities. Hydrogen was used as the test atmosphere because it was the purest gas available, and because little was known at that time of the formation of free uranium and its detrimental effects on tantalum cladding. The first specimen (No. 68) contained a W-UO_{2-x} core which was treated in uranium vapor to obtain a low oxygen-to-uranium ratio (1.85 to 1.90). Two other specimens tested at 2600°C (No. 101 and 108) contained cores which were sintered at 2400°C for 1 hour in hydrogen to yield oxygen-to-uranium ratios of 1.96 to 1.98. After testing for 10 hours at 2600°C, the condition of these specimens was generally poor.*† Minor blistering of the powder metallurgy cladding occurred on two specimens; all specimens developed several gas leaks, and the core - cladding reactivity varied from significant for the hydrogen-treated cores to gross for the uranium-impregnated core.

Two specimens of the Ta-clad W-UO₂ system were tested at 1930°C in purified helium to simulate the thermal conditions of the high-burnup experiment, 33MT115. Two enriched specimens of the design previously described under "Clad Fueled Specimen Fabrication" were tested for 270 and 1100 hours, respectively, at 1930°C. The first test was terminated because the specimen (No. M8E) was damaged in handling. Post-test inspection revealed no visual defects, no gas leaks, no significant alpha count, and only minor core - cladding reactivity.‡ The second specimen (No. M11E) was tested for 830 hours with no visible defects other than thermal etching. After an additional exposure of 270 hours, several gas leaks were detected at grain boundary separations. No surface radioactivity was detected by alpha counting and the core - cladding reactivity was moderate.§

Grain boundary separations were observed in several areas which penetrated approximately one-half of the cladding. An example of this condition is shown in Figure 2. 1-20. These results indicated that cladding failures were induced externally and occurred during the last test cycle.

All subsequent tests of the Ta-clad W-UO₂ system were conducted at 2200°C in an effort to determine long-time capabilities and, more recently, to resolve the gas leak problem which has been observed in long-time testing at 2200°C.

The gas leak problem was encountered during the fabrication of an enriched specimen for in-pile experiment LTFF-6. Eight specimens of this fuel element system developed gas leaks during a 2-hour proof-test at 2200°C in helium. All the W - 60UO₂ cores prepared for those specimens were sintered for 1 hour at 2500°C in hydrogen and were heated again at 2200°C for 1 hour in hydrogen after machining. One specimen (No. 113), which developed leaks during the 2-hour proof-test, was further tested at 2200°C to determine the effect of gas leaks on fuel loss. During 700 hours of testing in a static helium atmosphere, the specimen developed many more gas leaks and lost 0.7 gram of its original weight, or approximately 8 percent of its fuel. A typical leak in this specimen is shown in Figure 2. 1-21.

* "High-Temperature Materials Program Progress Report No. 21, Part B," GE-NMPO, GEMP-21B, April 23, 1963, p. 34.

† "High-Temperature Materials Program Progress Report No. 27, Part B," GE-NMPO, GEMP-27B, September 30, 1963, p. 48.

‡ Ibid., p. 51.

§ "High-Temperature Materials Program Progress Report No. 29, Part B," GE-NMPO, GEMP-29B, December 6, 1963, p. 50.

TABLE 2. 1-6
PROCESSING DATA AND TEST RESULTS ON Ta-CLAD W-UO₂ SPECIMENS

Specimen	Cladding Type ^a	Core Data				Density percent of theoretical	Oxygen-To-Uranium Ratio ^b	Cleaning Treatment ^c	Proof-Test Leak Check ^d	Bench-Test Conditions			Post-Test Inspection Results		
		Sinter Cycle		Atmosphere	Temperature, °C					Time, hr	Atmosphere	Visual Conditions	Leaks	Core - Cladding Reactivity	
		Temperature, °C	Time, hr												
68	PM	2400	1	U ^e	-	-	A	NT	2600	10	H ₂	Minor blistering	Several	Gross	
101	PM	2400	1	H ₂	93	-	A	NT	2600	10	H ₂	No defects	Several	Significant	
108	PM	2400	1	H ₂	94	-	A	NT	2600	10	H ₂	Minor blistering	Several	Significant	
M&E	AC	2500	1	H ₂	95	-	B	NT	1930	270	He	No defects	None	Moderate	
M11E	AC	2500	1	H ₂	96	-	B	NT	1930	830	He	Grain boundaries etched	None	-	
									1930	1100	He	Grain boundary separations	Several	Moderate	
113	PM	2500	1	H ₂	95	-	C	Leaked	2200	700	He ^f	Grain boundary separations	Many	Moderate	
119	PM	2500	1	H ₂	95	-	C	NT	2200	245	He ^f	No defects	End plate leak	Moderate	
121	PM	2500	1	H ₂	95	-	C	OK	2200	30	H ₂	No defects	Several	Minor	
122									2200	65	H ₂	No defects	Several	Minor	
126-128	AC	2500	1	H ₂	94	1.95	C	All leaked	NT	NT	NT	-	-	-	
134	PM	2200	1	H ₂	95	1.99	C	OK	2200	90	He ^f	Crack indications	Several	Minor	
135	PM		0.3	He	95	1.99	C	OK	2200	114	He ^f	Crack indications	Several	Minor	
137	AC	2000	1	H ₂	96	2.00	C	OK	2200	115	He ^f	Grain boundary deposit	Several	Minor	
138	PM								2200	110	He ^f	Scab deposits	Several	Minor	
139	PM	2500	0.3	He	96	2.00	C	OK	2200	90	He ^f	Scab deposits	Several	Minor	
142	AC	1800	1	H ₂	96	2.00	C	OK	2200	115	He ^f	Grain boundary deposit	Several	Minor	
145	PM								2200	80	He	Blister near weld	One over core	-	
146	PM	2500	0.3	He	96	2.00	C	OK	2200	299	He	Blister near weld	Leak in blister	-	
147	PM	2500	1	H ₂	93	1.97	C	OK	2200	493	He	Grain boundaries etched	Two over core	-	
148									2200	447	He	Grain boundaries etched	Leak near weld	-	
149									2200	140	He	No defects	Leak near weld	-	
162	PM	1800	1	H ₂	96	2.00	D	OK	2200	105	He	Blister near weld	Leak in blister	-	
163	PM		0.3	He	96	2.00	D	OK	2200	105	He	No defects	One over core	-	
168	PM	2500	1	He	88	2.01	E	OK	2200	67	He	Blister over core	Leak in blister	-	
169									2200	172	He	Blister over core	Leak in blister	-	
170	PM	2200	3	He	90	2.00	E	OK	2200	172	He	No defects	One over core	-	
171									2200	172	He	No defects	One over core	-	
172	PM	2200	5	U ^e	93	1.88	F	Leaked	NT	NT	NT	-	-	-	
173															

^aPM denotes powder metallurgy; AC is arc-cast

^bReported values are analytical results on UO₂ control samples sintered with the W-UO₂ cores.

^cCleaning treatment code: A is 1000°C - 15 min - vac.; B is 1650°C - 10 min - vac.; C is 2200°C - 1 hr. - H₂; D is 1300°C - 0.5 hr - H₂ plus 2200°C - 0.5 hr - He; E is 2200°C - 0.5 hr - He; F is 2200°C - 0.5 hr - H₂

^dNT - not tested

^eCores sintered in closed tungsten crucible containing uranium metal

^fStatic atmosphere

^gEach specimen received double sintering cycle as shown.

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Neg. 3796

100 X

Fig. 2.1-20—Photomicrograph of core-cladding interface of Ta-clad W-UO₂ specimen No. M11E which developed a leak after 1100 hours at 1930°C

Neg. 3795

100 X

Fig. 2.1-21—Photomicrograph of core-cladding area of Ta-clad W-UO₂ specimen No. 113 showing typical gas leak in the cladding which developed during testing at 2200°C in helium for 700 hours

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In contrast to the eight enriched fuel specimens, which leaked, six specimens (Nos. 119, 121, 122, 147, 148, and 149) were prepared by the same process and tested for more than 100 hours before developing leaks. Specimen No. 119 accumulated 120 hours with no defects and failed at some time before 245 hours when a single leak developed at a defect in the end plate cladding.* Specimen Nos. 147 and 148 were tested for 379 hours with no defects but did develop leaks during additional testing. The oxygen-to-uranium ratios of the fuel in these cores was estimated to be 1.95 to 1.97. Metallographic examination showed significant amounts of free uranium in the cores, and the data indicated that, at 2200°C, the uranium was available to react with the tantalum cladding.

A study of the effect of fuel stoichiometry on the formation of gas leaks was made using various experimental sintering cycles to produce W-UO₂ cores which should contain no free uranium. Oxygen-to-uranium ratios of 1.99 to 2.01 were obtained with no reduction in core density by sintering at lower temperatures (1800° to 2200°C).†‡ Although all of the specimens containing these experimental cores (Nos. 134 through 146) successfully passed the 2-hour proof-test, all but one developed leaks prior to 115 hours at 2200°C. Specimen No. 146 successfully completed 232 hours but leaked prior to 299 hours. To verify the detrimental effect of excessive amounts of free uranium, two specimens (Nos. 172 and 173) were prepared with an estimated oxygen-to-uranium ratio of 1.88 to 1.90. Both specimens exhibited gross failures after the 2-hour proof-test at 2200°C. The cladding on both specimens contained many fine cracks in addition to exhibiting many leaks, and metallographic examination revealed gross uranium - tantalum reactivity as shown in Figure 2. 1-22.

Neg. 3886

100 X

Fig. 2.1-22 - Photomicrograph of core-cladding interface of Ta-clad W-UO_{2-x} specimen No. 172 which leaked after 2-hour proof test at 2200°C. Free uranium from the core completely penetrated the tantalum cladding.

*Ibid., p. 53.

†Ibid., p. 41.

‡"High-Temperature Materials Program Progress Report No. 31, Part B," GE-NMPO, GEMP-31B, January 24, 1964, p. 24.

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The results of this study did not provide a solution to the leaking problem in the Ta-clad W-UO₂ specimens, but they did show that the amount of free uranium in the core is highly significant and that the fuel composition must be close to stoichiometric to increase fuel element life.

IN-PILE EVALUATIONS

A series of four in-pile tests of Ta-clad W-UO₂ fueled specimens was conducted in the LITR during CY-62 for times up to 1100 hours at maximum specimen temperatures of 1675°C. Based on these experiments, a new cartridge design capable of higher temperature operation was developed during the past year in which the specimen was contained within a series of five tantalum heat shields. Experiments LTFF-5 and LTFF-6 were of this design. Another type of experiment, intended to provide high-burnup data for the Ta-clad W-UO₂ system, was also designed and operated in the ETR at maximum specimen temperatures of 1930°C. However, this test (33MT115) was prematurely terminated because of excessive fission product release from one of the four specimens through a cladding defect.

In-Pile Experiment LTFF-5

The objective of this test was to demonstrate the time - temperature and fission product retention capabilities of the Ta-clad W - 60UO₂ fuel element system under simulated service conditions. This was the first in-pile test of a specimen containing agglomerated UO₂ and the first in-pile specimen to be gas-pressure-bonded. The specimen was clad with 0.51-millimeter-thick tantalum of powder metallurgy origin and was 1.27 centimeters in diameter, 3.81 centimeters in length, with a single axial hole 3.17 millimeters in diameter. The fuel loading was 5 grams of U²³⁵ in a W - 60UO₂ core. A sketch of the cartridge design is shown in Figure 2.1-23. The specimen and heat shields were instrumented with nine W / W - 26Re stranded-wire thermocouples. The thermocouples were insulated with BeO sleeving which limited the operating temperature to about 2350°C. The test cartridge was inserted in the C-48 facility of the LITR, and the test was conducted for one cycle of the reactor, about 178 hours. Special efforts were made to insure that the helium gas was of highest purity before it entered the capsule by passing it over hot (800°C) titanium chips which served as a getter for trace amounts of oxygen and nitrogen. A helium flow of about 85 liters per hour was maintained over the specimen. Charcoal traps were used at frequent intervals to sample the effluent gas for fission gas products. The specimen temperature was maintained at 1915°C for 176 hours. Before reactor shutdown, the specimen temperature was increased to 2200°C and held for 2 hours. During the 1915°C operation, the power generated by the specimen ranged from 24 to 30 watts/cm². The total burnup of U²³⁵ atoms was estimated to be 0.12 percent.

A summary of the fission gas release data obtained from analysis of eight charcoal traps is presented in Table 2.1-7. These data indicate that, during the 176-hour operation at 1915°C, no loss of fission gases occurred from the core of the specimen. The release values were so low they could be attributed to fuel contamination on the specimen surfaces. When the temperature was increased to 2200°C, the release of short-lived rare gases did not increase, but the release of Xe¹³³ did increase by a factor of four, to 1 x 10⁻⁵. This was attributed to diffusion through the cladding since post-test examination revealed no defects in the tantalum cladding.

When the test cartridge was disassembled, all components were in excellent condition including the thermocouples. The fueled specimen before and after testing is shown in the photographs of Figure 2.1-24. Measurements of the diameter of the specimen at several points were the same as pre-test measurements within the limits of accuracy of the hot cell technique.

Fig. 2.1-23—Schematic drawing of in-pile test cartridge for LTFF series showing Ta-clad W-UO₂ fuel element specimen contained in a series of five tantalum heat shields and all sealed in an Inconel can which contains the helium atmosphere.

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Neg. P63-1-15F

BEFORE TEST

Neg. RML 2086

AFTER TEST

Fig. 2.1-24—Tantalum-clad W-60UO₂ specimen of in-pile experiment LTFF-5 shown before and after testing at 1915°C for 176 hours and 2200°C for 2 hours

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TABLE 2.1-7
SUMMARY OF FISSION GAS RELEASE FROM TEST LTFF-5

Trap No.	Test Time, hr	Test Temperature, °C	Fraction Released (R/B) ^a				
			Kr ⁸⁷	Kr ⁸⁸	Kr ^{85m}	Xe ¹³⁵	Xe ¹³³
C-1	14	1920	6×10^{-7}	2×10^{-6}	3×10^{-6}	9×10^{-7}	6×10^{-7}
C-2	39.1	1900	4×10^{-7}	1×10^{-6}	1×10^{-6}	7×10^{-7}	9×10^{-7}
C-3	63.0	1920	3×10^{-7}	-	1×10^{-6}	2×10^{-6}	1×10^{-6}
C-4	88.3	1920	6×10^{-7}	8×10^{-7}	2×10^{-6}	1×10^{-7}	1×10^{-6}
C-5	137.7	1920	-	-	-	4×10^{-7}	-
C-6	160.1	1920	5×10^{-7}	1×10^{-6}	1×10^{-6}	2×10^{-6}	2×10^{-6}
C-7	175	1920	2×10^{-7}	-	2×10^{-6}	2×10^{-6}	3×10^{-6}
C-8	177.5	2200	9×10^{-7}	3×10^{-6}	3×10^{-6}	4×10^{-6}	1×10^{-5}

^aThe fraction of fission gases released (R/B) is defined as the ratio of the atoms released per second from the fuel element to the equilibrium production rate (atoms/second). Because of low count rates, the R/B values for Kr^{85m}, Kr⁹⁷, Kr¹⁸⁸, and Xe¹³⁵ are significant to a factor of 5; data for Xe¹³³ which was counted several days later are significant to a factor of 2.

The specimen was cut into eight sections which were used for both metallographic and radiochemical analyses. No significant core - cladding reactivity was observed in any of the polished sections, as shown in Figure 2.1-25. The only defect found in the core was a small circumferential crack in the tungsten matrix near the core - cladding interface. No significant loss in thickness of the tantalum cladding was detected, although one weak point was found in a welded joint of the center tube where excessive weld penetration had reduced the cladding thickness to less than 0.050 millimeter. However, this was apparently of sufficient thickness to contain the fuel and fission products. Although this specimen was clad with commercial grade sheet, and the tubing was prepared from powder metallurgy tantalum, none of the gross porosity which developed in the 2600°C laboratory tests of this material was observed in this in-pile specimen.

Radiochemical analyses performed on various portions of the test cartridge and the particle filter in the helium exit line indicated Ba¹⁴⁰, La¹⁴⁰, Ta¹⁸², and I¹³¹ were present, equivalent to fractional release values of 7×10^{-8} for Ba¹⁴⁰ and 6×10^{-8} for I¹³¹. These data were not absolute measurements of release, but they did indicate that the release of I¹³¹ and Ba¹⁴⁰ was no greater than that measured for rare gases collected in the charcoal traps.

In-Pile Experiment LTFF-6

Following the successful completion of experiment LTFF-5, the next experiment, LTFF-6, was scheduled to be operated at 2200°C using the same type of Ta-clad W-UO₂ fueled specimen and the same cartridge design. As explained in the section on "Clad Fueled Specimen Fabrication," the preparation of an enriched specimen for LTFF-6 was delayed by leaks in the tantalum cladding which developed during a 2-hour proof test at 2200°C. Eventually, the best specimen of a group of 14 was selected for the LTFF-6 assembly. This specimen had only a slight leak detectable by mass spectrometric inspection. The objectives of the experiment were amended, therefore, to obtain fission product release data as a function of time and temperature from a specimen with a known leak in the cladding. A secondary objective was to determine the acceptability of W / W-Re thermocouples as safety instru-

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Neg. R-525

OUTER TUBE SHELL
LONGITUDINAL SECTION

250 X

Neg. R-526

CENTER TUBE
LONGITUDINAL SECTION

250 X

GE-NMPO

Neg. R-511

CENTER TUBE
TRANSVERSE SECTION

100 X

Fig. 2.1-25 – Microstructures of typical core-cladding interface sections of in-pile test specimen LTF-5 after 176 hours at approximately 1915°C and 2 hours at 2200°C

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mentation for high-temperature in-pile tests. To accomplish these objectives, a progressive test program was scheduled to operate for one cycle of the LITR at several temperature levels up to 2200°C. The cartridge was inserted in the C-48 facility of the LITR toward the end of the year; at the close of the report period it had operated for 131 hours at 900°C, 136 hours at 1425°C, 273 hours at 1700°C, and was continuing operation at 1815°C. The fission gas release data obtained from charcoal traps taken at each temperature level indicated that the release of Xe¹³³ at 1425°C (R/B = 10⁻⁶) was equivalent to that released from LTFF-5 while operating at 1915°C. At 1700°C, however, the release of Xe¹³³ increased by a factor of three which gave the first indication of a significant release from the cladding defect. Analyses of the charcoal traps taken at 1815°C were not available for this report, but during steady state operation no excessive activity levels were detected. Operation of LTFF-6 is planned at temperatures up to 2200°C if such capability is indicated by fission product release data.

The nine W / W-Re thermocouples used in the inert gas section to instrument the specimen and heat shields were made of flexible stranded wire with BeO insulating sleeves. No lead wire was used with these thermocouples so that possible junction errors would be eliminated. Instead, the stranded thermocouple wire with ceramic insulation was run through flexible hose to the instrumentation cubicle. With the exception of one thermocouple which was open initially, this instrumentation proved reliable through the six cycles.

High Burnup Experiment 33MT115

Estimates are that the maximum burnup that can be achieved in 1000-hour LITR tests is about 0.2 percent of the U²³⁵ atoms. Data are needed for the stability of Ta-clad W-UO₂ fuel elements under conditions of much higher burnup, approximately 4 to 10 percent. To achieve this, a new specimen and cartridge were designed for use in the ETR facility at the National Reactor Testing Station. The thickness of the core was significantly reduced to allow a more uniform level of burnup. The configuration of this specimen and the fabrication of six enriched specimens were described in "Clad Fueled Specimen Fabrication."

The cartridge designed for this experiment is shown in Figure 2.1-26. Four specimens of Ta-clad W - 60UO₂ were contained in the cartridge, equally spaced around a 3.5-centimeter circle. Each specimen was contained in a stainless steel tube which was cooled externally by reactor water. Each of the four specimen tubes was connected to a common gas manifold for both inlet and exhaust helium gas. Two W / W - 26Re thermocouples with BeO insulation were located in the bore of each specimen adjacent to the fueled core.

The cartridge was inserted into the F-3 facility of the ETR where the flux was 7×10^{13} nv. With the objective of producing 5.3×10^{20} fissions/cm³, a burnup of approximately 12.5 percent of the 30-percent enriched fuel was required.* To accomplish this, the test was scheduled to run for 1250 hours at 1930°C. One of the specimens (No. 5) attained a temperature of 1925°C but, because of the flux profile in the facility, the other three specimens operated at 1700°C, 1600°C, and 1435°C.

The effluent helium - argon gas mixture was sampled by charcoal traps at 5 hours and 29 hours; no fission product activity was detected. A scram of the reactor occurred after 45 hours operation, and upon startup high radiation activity was detected at the test console which forced the test to be terminated.

Post-test examination in the hot cell at GE-NMPO revealed no evidence of deterioration or fuel specimen failure. Weight and dimensional measurements indicated no significant change in the specimens. Radiochemical analyses of leach solutions from each specimen for gross gamma count and isotopes showed that fission product release occurred from

*R. A. Pugh, "Test Request 33MT115," GE-NMPO, TM 63-5-2, May 1, 1963.

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Fig. 2.1-26—Cross-sectional view of cartridge assembly for in-pile test 33MT115 showing location of four fueled specimens, direction of gas flow and water coolant, and instrumentation with W / W - 26Re thermocouples (Dwg. 118C9691)

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specimen No. 5. When this specimen was sectioned and polished, two adjacent cracks were observed in the outer cladding, as shown in Figure 2.1-27.

Examination of longitudinal sections of this specimen failed to disclose any other indications of cladding failure and showed the general condition of the specimen to be sound. A large grain size was noted in the tantalum cladding, and the beginning of a core - cladding reaction was evident.

Fig. 2.1-27—Transverse section of Ta-clad W-UO₂ specimen No. 5 from in-pile test 33MT115, operated at 1925°C for about 45 hours, showing cracks in outer cladding which allowed release of fission products

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It was concluded that the release of fission products which caused the test to be terminated occurred through cracks in the outer cladding as shown in Figure 2.1-27. These cracks are similar to the grain boundary leaks found in laboratory test specimens discussed in the previous section and probably developed by the same mechanism which is not yet fully understood.

As soon as adequate control of the leaking problem is established, a new series of Ta-clad specimens will be prepared, and another attempt will be made to obtain the required high-burnup data from a long-time in-pile experiment.

REFRACTORY-METAL BRAZING INVESTIGATIONS

A development program for the brazing of refractory metals from 1900° to 2800°C was discussed previously.* Because of their high-temperature capabilities, tantalum and tungsten were the base metals evaluated. Table 2.1-8 tabulates results of specific braze alloy systems on these base metals.

Brazing Systems for Ta-Base Alloys

Nb-Ta-V (Melting Point < 2400°C) - Figure 2.1-28 shows the Nb-Ta-V ternary diagram. Generally, the braze alloys within the defined area of the ternary diagram show reasonable flow in brazing, moderate-sized fillets, and less than 0.010 centimeter erosion of the tantalum during the 5 minutes at brazing temperature. Figure 2.1-29 shows the typical microstructure of a braze alloy from this system. This system offers a choice of any brazing temperature between 2000° and 2400°C. No alloys within the defined area of the

Fig. 2.1-28 - Nb-Ta-V ternary diagram defining lines of constant brazing temperature

*"Second Annual Report - High-Temperature Materials and Reactor Component Development Programs, Volume I - Materials," GE-NMPO, GEMP-177A, February 28, 1963, pp. 45-47.

TABLE 2.1-8
REFRACTORY-METAL BRAZE ALLOY STUDIES
Part 1 - Brazing Alloys for Ta-Base Metal

Alloy No.	Composition, wt %	Cold ^a Workability	Brazing Temperature, °C	Fillet ^b Characteristics	Base Metal Erosion ^c	Fillet Microstructure
CB-4F	Nb - 5V	Erratic	2400	Medium	0.010 cm	Large grained
CB-4E	Nb - 10V	Erratic	2275	Medium	0.010 cm	Small voids
CB-4H	Nb - 15V	Erratic	2250	Large	None	Large grained
CB-4D	Nb - 20V	Erratic	2150	Medium	None	Large grained
CB-4I	Nb - 25V	Erratic	2125	Large	None	Large grained
CB-4C	Nb - 30V	Erratic	2100	Large	None	Fillet rough
CB-4J	Nb - 40V	Erratic	2000	Medium	None	-
CB-4K	Nb - 50V	Fair	1950	Medium	None	-
CB-46J	Nb - 10Ta - 30V	Erratic	2100	Medium	-	Large grained
CB-46H	Nb - 10Ta - 40V	Erratic	2100	Small	-	-
CB-46B	Nb - 20Ta - 20V	Fair	2400	Small	-	Several voids
CB-46G	Nb - 20Ta - 30V	Fair	2150	Small	-	-
CB-46I	Nb - 20Ta - 40V	Fair	2000	Small	-	Several small voids
CB-46C	Nb - 30Ta - 20V	Fair	2425	Small	None	-
CB-46F	Nb - 30Ta - 30V	Fair	2275	Medium	-	Several small voids
CB-46D	Nb - 40Ta - 25V	Fair	2400	Small	None	Several voids
CB-46E	Nb - 50Ta - 25V	Fair	2425	Small	None	Several small voids
CB-25F	Nb - 0.5Si	Good	2400	Small	None	Solid solution
CB-25E	Nb - 1Si	Fair	2375	Small	None	Slight second phase
CB-25D	Nb - 2Si	Brittle	2350	Medium	0.010 cm	Two-phase structure
CB-25C	Nb - 4Si	Brittle	2250	Small	0.010 cm	Two-phase structure
CB-25B	Nb - 7Si	Brittle	2000	Medium	None	Dendritic structure
TB-10D	Ta - 17Rh	Brittle	2200	Small	None	Large 2nd phase
TB-10C	Ta - 35Rh	Brittle	1900	Small	None	Heavy cracks
TB-13C	Ta - 48Ir	Brittle	2150	Small	None	Heavy cracks
CB-8C	Nb - 25Mo	Brittle	2400	Medium	None	Slight cracking
TB-4D	Ta - 20V	-	2425	Small	None	Slight 2nd phase
TB-25B	Ta - 3Si	Brittle	2425	Large	None	Slight 2nd phase
TB-5B	Ta - 70Nb	Excellent	2575	Small-even	None	Solid solution
TB-5C	Ta - 50Nb	Excellent	2600	Small-even	None	Solid solution
TB-5D	Ta - 30Nb	Excellent	2725	Small-even	None	Solid solution
TB-53B	Ta - 15Nb - 5Hf	Excellent	2775	Small-even	None	Solid solution
TB-53C	Ta - 15Nb - 10Hf	Excellent	2700	Small-even	None	Slight 2nd phase
TB-53D	Ta - 30Nb - 10Hf	Excellent	2625	Small-even	None	Slight 2nd phase
TB-53E	Ta - 50Nb - 10Hf	Excellent	2500	Small-even	None	Very slight 2nd phase
TB-53F	Ta - 70Nb - 10Hf	Excellent	2475	Medium-even	None	Very slight 2nd phase
TB-3F	Ta - 10Hf	Excellent	2825	Small-even	None	Slight 2nd phase
CB-3E	Nb - 30Hf	Excellent	2375	Medium-even	None	Moderate 2nd phase
CB-3F	Nb - 50Hf	Excellent	2275	Small-even	None	Heavy 2nd phase - one fillet crack
CB-2B	Nb - 10Zr	Very good	2375	Small-even	None	Slight 2nd phase
CB-2C	Nb - 15Zr	Very good	2300	Small-even	None	Moderate 2nd phase
CB-2D	Nb - 20Zr	Very good	2250	Medium-even	None	Heavy 2nd phase - cracks in fillet
CB-32B	Nb - 20Hf - 10Zr	Excellent	2275	Small-even	None	Moderate 2nd phase
CB-32C	Nb - 40Hf - 10Zr	Excellent	2175	Medium-even	None	Moderate 2nd phase
CB-32D	Nb - 30Hf - 20Zr	Excellent	2150	Medium-even	None	Cracking in 2nd phase
CB-62B	Nb - 30Ta - 30Zr	Very good	3200	Medium-even	None	Heavy 2nd phase - crack in joint
CB-62C	Nb - 30Ta - 15Zr	Very good	2400	Medium-even	None	Moderate 2nd phase
CB-62D	Nb - 15Ta - 15Zr	Very good	2375	Medium-even	None	Slight 2nd phase
CB-46K	Ta - 15Nb - 15V	Very good	2575	Blistered	None	Many fillet voids
CB-46L	Ta - 7Nb - 13V	Excellent	2800	Blistered	None	Many fillet voids
CB-46M	Ta - 5Nb - 10V	Excellent	2800	Blistered	None	Many fillet voids
WB-4E	W - 45V	Brittle	2400	Irregular	Severe	Many voids
WB-4F	W - 20V	Brittle	2760	Blistered	Severe	Many voids
WB-46B	Ta - 45W - 35V	Brittle	2700	Blistered	Severe	Many voids
WB-46C	Ta - 30W - 20V	Brittle	2760	Blistered	Severe	Many voids
WB-46D	Ta - 40W - 30V	Brittle	2700	Blistered	Severe	Many voids
WB-46E	Ta - 55W - 25V	Brittle	2760	Blistered	Severe	Many large voids
WB-46F	Ta - 20W - 15V	Brittle	2800	Irregular	Extreme	Many voids
WB-46G	Ta - 75W - 15V	Brittle	2800	Irregular	Extreme	Many voids

^a"Excellent" means complete reduction of casting to 0.025 cm sheet without intermediate anneal.

^b"Very good" means sheet split between 0.025 and 0.2 cm. Other comments refer to forged buttons.

^cFillet characteristics refer to visual judgment of fillet size and shape.

^d"None" means less than 0.007 cm of erosion into the base metal.

TABLE 2.1-8 (Cont.)
REFRACTORY-METAL BRAZE ALLOY STUDIES
Part 2 - Brazing Alloys for W-Base Metal (Cont.)

Alloy No.	Composition, wt %	Cold ^a Workability	Brazing Temperature, °C	Fillet ^b Characteristics	Base Metal Erosion ^c	Fillet Microstructure
MB-17B	Mo - 50Re	Excellent	2575	Small-even	None	Grain boundary precipitate
MB-17C	Mo - 40Re	Excellent	2575	Small-even	None	Grain boundary shrinkage voids
MB-9D	Mo - 15Ru	Forged okay	2400	Small-even	None	Two phase
MB-9E	Mo - 20Ru	Forged fair	2350	Small-even	None	Two phase
MB-9F	Mo - 30Ru	Poor	2200	Small-even	None	Two phase
MB-9G	Mo - 42Ru	Poor	1950	Small-even	None	Two phase
MB-179B	Mo - 10Re - 20Ru	Forged fair	2300	Small-even	None	Two phase
MB-179C	Mo - 10Re - 12Ru	Forged okay	2400	Small-even	None	Slight 2nd phase
MB-179D	Mo - 10Re - 15Ru	Forged fair	2350	Small-even	None	Two phase
MB-179E	Mo - 25Re - 20Ru	Poor	2300	Small-even	None	Two phase
MB-179F	Mo - 25Re - 15Ru	Forged fair	2300	Small-even	None	Two phase
MB-179G	Mo - 20Re - 15Ru	Poor	2325	Small-even	None	Two phase
MB-179H	Mo - 20Re - 12Ru	Forged fair	2400	Very small	None	Two phase
MB-179I	Mo - 10Re - 10Ru	Forged fair	2425	Very small	None	Slight 2nd phase
MB-179J	Mo - 10Re - 35Ru	Brittle	1950	Small-even	-	Wide melting range
MB-179K	Mo - 25Re - 25Ru	Brittle	1950	Small-even	-	Wide melting range
MB-179L	Mo - 48Re - 10Ru	Brittle	2400	Small-even	-	Wide melting range
MB-179M	Mo - 40Re - 15Ru	Forged fair	2250	Medium-even	None	Eutectic structure
MB-10B	Mo - 43Rh	Forged okay	1950	Small-even	0.007 cm	Small 2nd phase dispersion
MB-10C	Mo - 20Rh	Poor	2300	Small-even	None	Two phase
MB-10D	Mo - 15Rh	Brittle	2350	Small-even	None	Two phase
MB-10E	Mo - 35Rh	Forged fair	1950	Medium-even	-	-
MB-1710B	Mo - 30Re - 15Rh	Brittle	2300	Small-even	0.007 cm	Eutectic structure
MB-1710C	Mo - 30Re - 20Rh	Forged good	2175	Small-even	None	Eutectic structure
MB-1710D	Mo - 45Re - 12Rh	Forged good	2275	Small-even	0.007 cm	Eutectic structure
MB-1710E	Mo - 20Re - 20Rh	Forged fair	2250	Small-even	0.007 cm	Eutectic structure
MB-1710F	Mo - 20Re - 15Rh	Forged fair	2350	Small-even	-	-
MB-1710G	Mo - 20Re - 27Rh	Forged good	2150	Small-even	0.012 cm	Eutectic structure
MB-1710H	Mo - 10Re - 33Rh	Forged good	1950	Small-even	0.007 cm	Very fine 2nd phase
MB-1710I	Mo - 10Re - 20Rh	Poor	2300	Very small	None	Slight 2nd phase
MB-14B	Mo - 45Pt	Forged excellent	2050	Small-even	None	Two phase
MB-1714B	Mo - 45Re - 15Pt	Brittle	2350	Small-even	None	Two phase
MB-1714C	Mo - 30Re - 25Pt	Forged good	2200	Medium-even	-	-
MB-1714D	Mo - 20Re - 10Pt	Forged fair	2350	Small-even	None	Heavy 2nd phase
MB-1714E	Mo - 10Re - 40Pt	Forged excellent	2050	Small-even	-	-
MB-11B	Mo - 65Pd	Forged excellent	1825	Irregular	Extreme	Extreme grain boundary damage
MB-11C	Mo - 50Pd	Forged excellent	2050	Irregular	Extreme	Extreme grain boundary damage
MB-1711B	Mo - 50Re - 15Pd	Brittle	-	-	-	Dropped
MB-1711C	Mo - 30Re - 30Pd	Forged good	-	-	-	Dropped
MB-1711D	Mo - 10Re - 40Pd	Forged excellent	2100	Irregular	Extreme	Extreme grain boundary damage
MB-177B	Mo - 40Re - 20Cr	Forged good	2550	Blistered	-	Severe Cr evaporation
MB-177C	Mo - 37Re - 25Cr	Forged good	2550	Blistered	None	Severe Cr evaporation
MB-177D	Mo - 35Re - 30Cr	Forged fair	2550	Blistered	-	Severe Cr evaporation
MB-177E	Mo - 30Re - 25Cr	Forged good	2550	Blistered	-	Severe Cr evaporation
WB-178B	Mo - 50Re - 5W	Excellent	2625	Small-even	None	Solid solution
WB-178C	Mo - 49Re - 10W	Excellent	2625	Small-even	None	Solid solution
WB-178E	Mo - 45Re - 10W	Excellent	2600	Small-even	None	Solid solution
WB-178F	Mo - 40Re - 20W	Very good	2650	Small-even	None	Very slight dispersion
WB-178G	Mo - 35Re - 30W	Very good	2800	Very small	None	Solid solution
WB-178H	Mo - 40Re - 30W	Very good	2750	Medium-even	None	Solid solution
WB-178I	Mo - 46Re - 30W	Excellent	2800	Small-even	None	Slight two phase
WB-14D	W - 50Pt	Forged excellent	2400	Small-even	0.010 cm	Two phase
WB-25B	W - 4Si	Brittle	2450	Irregular	Extreme	Heavy evaporation
WB-25C	W - 5Si	Brittle	2450	Irregular	Extreme	Heavy evaporation
WB-1725B	W - 20Re - 4Si	Brittle	2450	Irregular	Extreme	Heavy evaporation

^a"Excellent" means complete reduction of casting to 0.025 cm sheet without intermediate anneal.

^b"Very good" means sheet split between 0.025 and 0.2 cm. Other comments refer to forged buttons.

^cFillet characteristics refer to visual judgement of fillet size and shape.

^d"None" means less than 0.007 cm of erosion into the base metal.

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Fig. 2.1-29—Nb—25V braze alloy on Ta-base metal brazed at 2125°C in hydrogen

ternary contained embrittling phases, and no second phases were formed during the diffusion of these alloys into the Ta-base metals. In addition, alloys initially containing higher percentages of tantalum have comparatively rapid remelt temperature increases as the solidus temperature rises rapidly with the addition of tantalum by diffusion. The major difficulty with this system at present is the erratic deformation behavior experienced during the cold fabrication of sheet and wire. Fabrication and alloy modifications are being investigated in an attempt to eliminate this problem.*

Other Braze Systems Investigated for Ta-Base Alloys - Other brazing systems investigated include the following:

1. Nb-Si - Successful braze joints were achieved with various amounts of silicon (from 0.5 to 7 weight percent). Figure 2.1-30 shows a joint made with Nb - 7Si.
2. Ta-Nb-Hf - This system with 0 to 10 weight percent hafnium is being evaluated as a brazing system for Ta - 10W between 2475° and 2825°C.
3. Ta-Nb-V and Ta-W-V (Melting Point > 2400°C) - No further work is planned due to severe vaporization of the braze alloy.
4. Nb-Hf, Nb-Zr, Nb-Hf-Zr, and Nb-Ta-Zr - See Table 2.1-8 for the characteristics of these systems.
5. Others - Other alloys evaluated included Nb - 25Mo, Nb - 20 to 50Hf, Ta - 20V, Ta - 25 to 32Hf, Ta - 3Si, and Ta - 5 to 10Hf - 1 to 3Si. Certain alloys from these systems may be considered at a later date for very high-temperature brazing of Ta-base alloys.

Brazing Systems for W-Base Alloys

The following systems were evaluated for brazing W-base alloys:

1. Mo-Re - Brazing trials were made with Mo - 40 and 50Re on W - 25Re-base metal. Both compositions can be cold-rolled to sheet from arc-cast buttons. Both alloys also form even fillets with good flow characteristics and little erosion of the base

*"High-Temperature Materials Program Progress Report No. 31, Part B," GE-NMPO, GEMP-31B, January 24, 1964, pp. 37-38.

SECRET

Neg. 3042

ETCHED, 30 LACTIC 10HNO₃ - 10Hf

75 X

Fig. 2.1-30-Nb-7Si braze alloy on Ta-base metal brazed at 2000°C in hydrogen

metal at 2575°C. A heavy grain boundary precipitate was noted in fillets of Mo - 50Re. The Mo - 40Re alloy formed single-phase fillets but showed solidification shrinkage where grain boundaries came to the surface of the fillets. Figure 2.1-31 shows W - 25Re-base metal brazed with Mo - 50Re in hydrogen at 2575°C.

2. Mo-Re-Ru - The ternary diagram in Figure 2.1-32 shows the specific alloys of this system that were investigated for brazing tungsten and molybdenum alloys between 1950° and 2400°C. The brazing isotherms shown in the diagram are derived from the melting point determinations of specific alloys represented as black dots. Studies showed that all alloys formed good joints, although two alloys did not exhibit good rolling characteristics. Figure 2.1-33 shows a representative joint made from alloys of this system.
3. Mo-Re-Rh - The alloys under investigation are shown in Figure 2.1-34 as black dots on the ternary diagram. Figure 2.1-35 is a photomicrograph of a W-base metal brazed with Mo - 30Re - 20Rh in hydrogen at 2150°C.
4. Mo-Re-W - Figure 2.1-36 shows a representative joint made from one of these alloys.
5. Mo-Re-Cr - Initial brazing trials indicated chromium vaporized from the braze alloy; no additional work is planned on this system.
6. Mo-Re-Pt - Figure 2.1-37 shows a braze joint in the W-base metal made with one of these alloys.
7. Mo-Re-Pd - A severe grain boundary attack of the tungsten by the brazing alloy was noted as far as 0.5 centimeter from the joint area. Figure 2.1-38 shows this attack. No further work is planned with this system.
8. W-Pt - A peritectic reaction within the W-Pt binary diagram limits this system to a maximum operating temperature of 2400°C when brazing W-base metal.

SECRET

Neg. 3127

ETCHED

75X

Fig. 2.1-31 - Mo-50Re braze alloy on W-25Re base metal brazed at 2575°C in hydrogen

Alloys for Brazing Tantalum to Tungsten

Several indications of joint embrittlement were noted in tantalum-to-tungsten joints when Nb-V brazing alloys were used.* A study was made to determine if this tendency existed. The following results were noted:

1. Ta-Ta joints brazed with Nb - 10V and pure niobium were the same as those seen during the preliminary screening; nothing unusual was apparent, and there was no evidence of embrittlement. As-brazed and vacuum-annealed joints appeared to be identical.
2. Ta-W joints brazed with Nb - 10V and pure niobium showed evidence of discontinuities or separations at the tungsten - braze-alloy interface and in grain boundaries of the brazing alloy leading from this interface. There was no evidence of cracking in the tungsten. A vacuum anneal neither relieved nor magnified this tendency. There were also several locations in joints brazed with pure niobium where grains of braze alloy adjacent to the tungsten interface had completely chipped away from the tungsten.
3. Ta-Ta and Ta-W joints brazed with Mo-Re showed no evidence of cracking or tantalum - braze-alloy interface separation. The Mo-Re fillets showed only the shrinkage voids characteristic of large fillets of this braze alloy. A discontinuity or separation, if it occurred at all, would be expected to occur at the tantalum - braze-alloy interface. This interface showed a diffusion zone but no evidence of embrittlement nor separation. Vacuum annealing widened the diffusion zone but caused no other change. Thermal contraction has some effect on cracking tendencies so that a final analysis of the usefulness of Mo-Re would have to be based upon strength measurements.

* "High-Temperature Materials Program Progress Report No. 23, Part A," GE-NMPO, GEMP-23A, May 31, 1963, pp. 21-22.

SECRET

Fig. 2.1-32 - Brazing alloys from the Mo-Re-Ru system

Neg. 3131

ETCHED

75X

Fig. 2.1-33 - Mo-10Re-12Ru braze alloy on W-25Re-base metal brazed at 2350°C in hydrogen

SECRET

Fig. 2.1-34 – Brazing alloys from the Mo-Re-Rh system

Neg. 3293

UNETCHED

75X

Fig. 2.1-35 – Mo-30Re-20Rh braze alloy on W-base metal brazed at 2150°C in hydrogen

SECRET

Neg. 3296

UNETCHED

75X

Fig. 2.1-36—Mo—30W—40Re braze alloy on W-base metal brazed at 2750°C in hydrogen

Neg. 3294

UNETCHED

75 X

Fig. 2.1-37—Mo—45Pt braze alloy on W-base metal brazed at 2100°C in hydrogen

SECRET

Neg. 3295

UNETCHED

75X

Fig. 2.1-38 - Mo-10Re-40Pd braze alloy on W-base metal brazed at 2100°C in hydrogen

SUMMARY AND CONCLUSIONS

Latest sintering data indicate that 2200°C is an adequate temperature for sintering W - 60UO₂ in hydrogen. In 1 hour under these conditions, 95 to 96 percent of theoretical density was achieved; fuel losses averaged 43 mg/cm², and the oxygen-to-uranium ratio was about 2.00 (± 0.01).

The addition of 10 weight percent ThO₂ to UO₂ raised the melting point of the fuel more than 100°C. Core specimens of W - 48UO₂ - 12ThO₂ were heated at 2800°C for 1 hour in hydrogen and at 2900°C for 5 minutes in helium with no melting nor fuel reaction. Adding ThO₂ to W-UO₂ cores reduced fuel loss rates at 2400°C by a factor of 2.5.

The thermal expansion measurements of W - 60UO₂ up to 2200°C show 2.1 percent expansion compared to 1.8 percent for tantalum. Similar measurements were made for various other core compositions and cladding materials. The thermal conductivity of W - 60UO₂ containing agglomerated UO₂ particles was determined as 0.21 watt/cm-°C at 2250°C, while UO₂ was about 0.045 watt/cm-°C at the same temperature. The enthalpy of W - 60UO₂ at 2200°C was measured as 118 cal/g. The rupture strength of W - 60UO₂ at 2260°C for 1 hour was about 50 kg/cm² in hydrogen and 82 kg/cm² in helium, with elongations ranging from 5 to 10 percent.

The quality of thin-wall tubing of commercial Ta, Ta - 10W, Nb, W-Re, and Mo was inadequate for fuel element cladding requirements. Encouraging progress was made by working closely with tubing vendors, and specifications were proposed which markedly reduced the incidence of defects in the most recent shipments of tantalum tubing.

The fabrication of Ta-clad W-UO₂ in-pile specimens to extremely close tolerances was accomplished, and the sealing of tantalum cladding by gas-pressure diffusion-bonding proved to be entirely satisfactory.

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Laboratory evaluations were performed on 75 specimens representing five different fuel element systems to determine their maximum time - temperature capabilities. Specimens of the W-Re-clad W-UO₂-ThO₂ system were tested at 2800°C for 10 hours and 2900°C for 1 hour in hydrogen with no detrimental effects. This system proved to be greatly superior to all others evaluated to date. Nine specimens of the Ta-clad W-UO₂-ThO₂ system were tested at 2200°C in helium. All remained leak-free for at least 300 hours, and five are still on test. One, which has accumulated 1278 hours, still shows good stability. Evaluations of the Ta-clad W-UO₂ system were concerned with resolution of the gas leak problem and the effect of fuel stoichiometry on the formation of gas leaks at 2200°C. The cause of leaks was primarily free uranium metal which permeated the grain boundaries of tantalum cladding in a few hours at 2200°C if the oxygen-to-uranium ratio of the fuel was less than 2.00. Maximum leak-free test time for a specimen was 379 hours at 2200°C. One specimen of the Mo-clad W-UO₂ system was tested at 2400°C for 100 hours in hydrogen with only moderate core - cladding reactivity. Three specimens of the Nb-clad Mo-UO₂ system were tested for 1019 hours at 1800°C in helium with no external defects and no gas leaks at the end of the year.

Three in-pile experiments were conducted using Ta-clad W-UO₂ specimens. High burn-up test 33MT115 in the ETR was aborted after 45 hours at a maximum specimen temperature of 1925°C because of excessive airborne fission products. The leaks were located in the hottest of the four specimens and appeared to be intergranular failure.

Experiment LTFF-5 was successfully operated in the LITR for 176 hours at 1915°C and 2 hours at 2200°C with no abnormal activity detected and no appreciable core - cladding reactivity. Experiment LTFF-6 was conducted as a study of fission gas release from a specimen with a known leak. A stepwise heating cycle was followed. The experiment was scheduled to continue at 1815°C and up to 2200°C if such capability was indicated by fission product release data. Preliminary analyses of fission gas release at 1700°C gave the first indications of significant gas release from the cladding defect.

A considerable number of potential brazing systems has been investigated for the refractory metals and pertinent brazing characteristics for these systems have been reviewed. Systems are available that offer a choice of any brazing temperature between 1900° and 2800°C for any of the refractory metals.

PLANS AND RECOMMENDATIONS

The study of core sintering techniques will be continued to establish an optimum treatment for the required physical and chemical stability of both W-UO₂ and W-UO₂-ThO₂ cores.

The determination of physical and mechanical properties of various core compositions and cladding materials will continue at temperatures up to 2500°C.

Improvements in the quality of refractory-metal tubing and cladding materials will be encouraged through cooperative efforts with vendors and the establishment of specifications for materials of fuel element quality.

Laboratory tests will be conducted for several refractory-metal systems with emphasis on long-time (1000-hour) capabilities at temperatures of 1800° to 2400°C.

In-pile experiments will be conducted in both the LITR and ETR with emphasis on W-Re-clad specimens and the effects of high burnup on fuel element stability.

Pertinent mechanical and metallurgical operating characteristics will be determined for selected braze-alloy - base-metal combinations. A procedure will be established for comparing several brazing alloys to aid in choosing an alloy for specific applications. Brazing alloy systems will be established for rhenium and rhenium-base alloys.

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2.2 OXIDATION-RESISTANT FUEL ELEMENT MATERIALS RESEARCH (57001)

The objective of this program is to produce and evaluate fuel element materials capable of long-time service in oxidizing atmospheres at high temperatures ($>1000^{\circ}\text{C}$) with negligible fission fragment release.

The progress during the past year on oxidation-resistant fuel element materials research is discussed under the following headings: (1) Fuel Materials Evaluations, (2) Fuel Element Cladding Alloy Development and Fabrication, and (3) Cladding Evaluations in Steam.

FUEL MATERIALS EVALUATIONS

Because of its excellent oxidation resistance Fe - 25Cr - 4Al - 1Y alloy* is being studied as a possible fuel element cladding material for both air-cooled and superheated steam reactors. When used with Fe-Cr-Al-Y, uranium dioxide, the conventional nuclear fuel for high-temperature reactors, has a tendency to be reduced at high temperatures by the aluminum in the alloy, thereby permitting uranium to migrate to the cladding surface. To overcome this tendency, various means of stabilizing UO_2 have been investigated. Also, three other uranium compounds (US, UF_3 , and UN) were investigated for possible better stability with Fe-Cr-Al-Y. All fuel materials evaluation was based on the concept of a fuel element with the uranium compound dispersed in a metal matrix.

Uranium Dioxide

Pressed and sintered cores of UO_2 dispersed in the matrix metal were clad with Fe-Cr-Al-Y using the two specimen configurations shown in Figure 2.2-1. The fuel compound UO_2 was tested as a dispersion in both chromium and iron matrices and in combination with Cr_2O_3 as a barrier-former, or with ThO_2 as a stabilizing addition.

UO_2 - Cr_2O_3 Barrier Study - Work performed in CY-62[†] indicated that the addition of about 2 volume percent Cr_2O_3 to the Cr - 50 UO_2 core compact clad with Fe-Cr-Al-Y served as a source of oxygen to form a thin barrier of Al_2O_3 at the interface of core and cladding.

To evaluate the stability and effectiveness of the Al_2O_3 barrier in long-time tests at 1250°C , a series of capsule specimens was fabricated using Fe-Cr-Al-Y tubing machined from rods. Cores were prepared of blended Cr - 50 UO_2 - 2.4 Cr_2O_3 (vol %) and sintered in a double cycle of 1300°C in hydrogen and 1600°C in helium. This cycle was designed to sinter to a useful density without reduction of the Cr_2O_3 ; 92 percent of theoretical density was achieved. These cores were machined to fit tightly in the 9.5-millimeter-diameter tubing and the ends were faced to a length of 19 millimeters. End plugs were TIG-welded in an argon-filled dry box; after inspection for gas leaks, the specimens were gas-pressure-bonded at 1100°C under 700 kg/cm^2 helium pressure for 1 hour. Three specimens in which the cladding was well-bonded to the cores were tested for 186 hours at 1000°C , 226 hours at 1150°C , and 50 hours at 1250°C . All developed blisters in the cladding and a rupture occurred in the specimen tested at 1000°C . Metallographic examination disclosed that the Al_2O_3 barrier was about 5 microns thick in the 1150°C specimen and about 9 microns thick in the 1250°C specimen. However, similar specimens of Cr - 50 UO_2 tested under the same conditions without the Cr_2O_3 additive, also formed an interface barrier (Figure 2.2-2) adequate to prevent uranium diffusion through the cladding. The barrier, about 5 microns thick, formed in 50 hours at 1250°C . The addition of Cr_2O_3 was not necessary, therefore, to form the Al_2O_3 interface.

*Unless otherwise noted, all core compositions are in volume percent; all cladding compositions are in weight percent.

[†]"Second Annual Report - High-Temperature Materials and Reactor Component Development Programs, Volume II - Materials," GE-NMPO, GEMP-177B, February 28, 1963, pp. 190-193.

SECRET

DIMENSIONS IN CENTIMETERS

Fig. 2.2-1 - Configuration of two types of Fe-Cr-Al-Y specimens used for laboratory evaluations of fuel compounds

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Neg. 2083

250 X

Fig. 2.2-2 - Microstructure of Fe-Cr-Al-Y-clad Cr-50UO₂ specimen after testing for 50 hours at 1250°C, showing 5-micron-thick barrier of Al₂O₃ formed at the interface

Cr - 50UO₂ Cores - The core structure of the Fe-Cr-Al-Y-clad Cr- 50UO₂ specimen shown in Figure 2.2-2 is predominantly a continuous UO₂ phase with large chromium particles distributed throughout. A more desirable structure is that of a continuous metal matrix surrounding the fuel particles. Such an improved core structure was achieved by the use of agglomerated UO₂ particles of 75- to 150-micron size as shown in Figure 2.2-3. Specimens containing agglomerated UO₂ and specimens containing the fuel in the form of a fine powder were tested for stability. The results of these tests are given in Table 2.2-1. Under metallographic examination the alumina barrier thickness varied from 3.8 to 6.6 microns. Although no uranium diffusion was evident in either type of specimen, the interface barrier was more uniform in the specimens containing agglomerated UO₂, as shown in Figure 2.2-3.

As a further test for uranium diffusion in the Fe-Cr-Al-Y-clad Cr - 50UO₂ system, a series of die specimens was prepared with cores containing agglomerated UO₂, UO₂ powder, and UO₂ stabilized with 22 percent ThO₂.

These cores were sintered in hydrogen for 1 hour at 1500°C, then loaded into the die specimens and hot-pressed in argon at 1150°C under a load of 160 kg/cm² to densify the core and to insure a bond. Hot-pressing effectively upset the punch sufficiently to seal the core into the die specimen. The face of the die was then machined to a calculated cladding thickness of 0.89 millimeter. The die specimens were then heated in static air at 1250°C and removed from the furnace after 224, 627, 824, and 1279 hours to analyze the machined face for uranium intensity using X-ray fluorescence techniques. These results are shown in Figure 2.2-4. These data represent the average of two specimens of each of three types of UO₂ fuel, and one specimen containing Cr₂O₃ which was run in the same test for comparative purposes. These data show that the agglomerated UO₂ particles are more stable than the fine UO₂ powder and that the addition of ThO₂ may result in improved stability. This series of die specimens was still on test at the end of the year;

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Fig. 2.2-3 - Microstructure of Fe-Cr-Al-Y-clad Cr-50UO₂ specimen after testing for 50 hours at 1250°C, showing agglomerated particles of UO₂ in chromium matrix and more uniform Al₂O₃ barrier at the interface

TABLE 2.2-1

RESULTS OF STABILITY TESTS OF Fe-Cr-Al-Y-CLAD Cr-UO₂ SPECIMENS^a

Core Composition, vol. %	Core Density, Percent of Theoretical	Test Conditions ^b		Results		
		Temperature, °C	Time, hr	Surface Condition	Uranium Diffusion	Barrier Thickness, microns
Cr - 50UO ₂ (powder)	92 ^c	1250	50	Excellent ^d	None observed	5.1
	92	1150	226	Excellent	None observed	6.6
	92	1000	500	Excellent	None observed	-
Cr - 50UO ₂ (agglomerated)	79	1250	50	Excellent	None observed	5.1
	80	1150	226	Excellent	None observed	3.8

^aSpecimens are 1.05 centimeters in diameter and 2.54 centimeters long with 0.51 millimeter of autoclave-bonded cladding.

^bTested in slow moving air.

^cAll cores sintered at 1500°C for 1 hour in hydrogen.

^dExcellent surface condition indicates adherent grey coating formed.

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Fig. 2.2-4—Relative uranium intensity on surface of Fe-Cr-Al-Y-clad die specimens with various core compositions tested at 1250°C in air

additional specimens of the same core compositions were added to this 1250°C test series. In a new series of die specimens of the same types, tested at 1100°C after 450 hours, no visual evidence of uranium diffusion in the nature of dark surface oxide had been observed. A reliable indication of uranium diffusion is a darkening of the cladding over the core due to the formation of U₃O₈ in combination with the normal light grey alumina protective film which is characteristic of the Fe-Cr-Al-Y alloy.

Fe - 50UO₂ Cores.— Experimental core compacts of Fe - 50UO₂ (vol %) were prepared using both as-received UO₂ powder and agglomerated UO₂ particles. These fuels were blended with electrolytic or carbonyl iron powder and cold-pressed at 2800 kg/cm² to a green density of 63 to 67 percent of theoretical. After sintering for 2 hours at 1200°C in hydrogen (0°C dewpoint), no appreciable increase in density was realized. Cold-pressing the sintered body in a steel die at 4200 kg/cm² did not increase the density appreciably. In view of these initial results, a study of sintering variables was initiated toward the end of the year in an effort to produce high-density Fe-UO₂ cores. A series of low-density cores was machined to fit Fe-Cr-Al-Y capsules of the configuration described previously, under "UO₂-Cr₂O₃ Barrier Study." The end plates of the capsules were sealed by TIG-welding and the specimens were gas-pressure-bonded in an autoclave at 1100°C under 700 kg/cm² of helium. This processing reduced the diameter of the capsules as much as 1 millimeter, indicating the final density of the fuel core should be about 90 percent of theoretical, although no actual measurement of final density was possible without destroying the specimen.

After inspection for core - cladding bond and gas leaks, four sound specimens of Fe-Cr-Al-Y-clad Fe-UO₂ were tested at 1250°C in slow flowing air. Two capsule specimens containing Fe-Cr-Al-Y-clad Cr - 50UO₂ were included in the test for comparative purposes. One of each type of specimen failed early due to cladding defects, but the remaining three Fe - 50UO₂ and one Cr - 50UO₂ remained on test for 1043 hours with no discoloration of the normal hard grey surface oxide on the cladding.

Metallographic examination of sections of these specimens revealed excellent bonding of the Fe-Cr-Al-Y cladding to the Fe core matrix, with a uniform surface oxide layer; the Cr core matrix specimen showed the development of a barrier at the interface as observed in previous Fe-Cr-Al-Y-clad Cr-UO₂ specimens. The microstructure of the Fe-Cr-Al-Y-clad Fe - 50UO₂ specimen containing agglomerated UO₂ is shown in Figure 2.2-5. The

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Fig. 2.2-5—Microstructure of Fe-Cr-Al-Y-clad Fe-50UO₂ capsule specimen tested at 1250°C in slow moving air for 1043 hours

photomicrograph shows that an excellent metallurgical bond was attained between the Fe core and Fe-Cr-Al-Y cladding by processing in the autoclave; furthermore, no gross reaction product occurred at the interface. The use of agglomerated UO₂ particles produced the desired continuous metal matrix with a relatively high fuel loading. The Fe-Cr-Al-Y cladding shows the usual excellent oxidation resistance after 1000 hours at 1250°C. Electron-microprobe analysis will be used to determine if free uranium metal is present either in the UO₂ fuel particles or in the cladding.

Uranium Monosulfide

Uranium monosulfide was investigated as an alternative fuel. Initial tests indicated that US was stable with Fe-Cr-Al-Y cladding to at least 1250°C if an oxygen-free material were used. Therefore, efforts were continued to improve the production method for high-purity US. A series of test specimens was prepared to evaluate the material stability in a fuel element.

Preparation of US - A detailed procedure for the preparation of uranium monosulfide was presented in a previous report.* Briefly, this method consists of heating uranium hydride in flowing H₂S gas to form US₂ and then reducing US₂ to US by reacting at high temperatures with uranium. Essentially stoichiometric US was produced, but traces of UOS and/or U₂S₃ were detected in all batches. The source of oxygen was traced to the H₂S gas, three lots of which were rejected for high oxygen contents (~1.5%). A chemically pure grade of H₂S was obtained in which the percentages of major impurities were 0.3 CO₂, 0.2 COS, 0.3 CS₂, and less than 0.1 SO₂. A batch of US₂ was prepared using this new gas; the US₂ was then reacted with uranium powder at 1900°C in hydrogen, yielding US which was analyzed as 11.94 percent sulfur (stoichiometric composition, 11.86% S) with an oxygen content of 0.10 percent. This represented a considerable improvement over previous products which contained as much as 0.71 percent oxygen. The major phase was identified as US with traces of U₂S₃ and UOS by X-ray diffraction analysis. The reacted

*"High-Temperature Materials Program Progress Report No. 19, Part B," GE-NMPO, GEMP-19B, January 25, 1963, p. 69.

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material was crushed and screened in an argon-filled dry box to provide -325 mesh powder for fueled specimens.

Fe-Cr-Al-Y-Clad Cr-US - Specimens of both the capsule and the die types were prepared to evaluate US as a fuel compound for use with Fe-Cr-Al-Y alloy. Early specimens prepared using the US with high-oxygen content developed a dark surface layer characteristic of uranium diffusion after 25 hours at 1250°C, and the microstructure showed a grey phase identified as UOS, at the core - cladding interface.

When the high-purity US became available, die specimens were prepared using sintered compacts of US and Cr - 50US (vol %). These core compacts were sintered for 1 hour at 1500°C in hydrogen; the Cr-US composition achieved a theoretical density of 93 percent and the US compact a theoretical density of 90 percent. These cores were loaded in Fe-Cr-Al-Y dies and hot-pressed in argon at 1150°C with a load of 160 kg/cm² applied to the punch. This was sufficient to deform the punch and die and insure intimate contact of the fuel with the cladding. These specimens were tested at two temperatures, 1100°C and 1250°C; Fe-Cr-Al-Y-clad Cr - 50UO₂ specimens were tested at the same time for comparative purposes. At year's end, 617 hours of test time had been accumulated at 1250°C and 840 hours at 1100°C. No visual evidence of uranium diffusion in the nature of a dark surface oxide was noted on any of the specimens tested at 1100°C, and X-ray fluorescence measurements made at 715 hours showed no significant uranium contamination. Three specimens tested at 1250°C were also measured for uranium intensity after three time intervals; results of these tests are presented in Table 2.2-2.

TABLE 2.2-2

RELATIVE URANIUM INTENSITY^a OF
THREE SPECIMENS TESTED AT 1250°C

Core Composition, vol. %	Inspection Intervals		
	329 hr	452 hr	617 hr
Cr - 50US	35	46	63
US	46	61	75
Cr - 50UO ₂	1	3	5

^aMeasured by X-ray fluorescence

Data obtained to date indicate that high-purity US may be sufficiently stable for use at temperatures up to 1100°C, but that at 1250°C, US is more readily reduced than UO₂.

These specimens will continue on test for at least 1500 hours with periodic measurements of uranium intensity on the surface of the Fe-Cr-Al-Y cladding. Additional capsule-type specimens containing US fuel were prepared and will be tested over a range of temperatures in comparison with specimens containing UO₂.

Uranium Trifluoride

Uranium trifluoride (UF₃) was prepared by reacting UF₄ with uranium hydride in a tungsten crucible heated in argon for 1 hour at 1050°C and 0.5 hour at 1500°C. The product was black and cake-like in appearance and was easily crushed to powder. Chemical analyses indicated 79.9 percent uranium (stoichiometric UF₃ contains 80.68% U) and 0.47 percent oxygen. Another batch was produced by the hydrogen reduction of UF₄ at 1000°C but this method proved to be slow and unsatisfactory.

During attempts to sinter compacts of the best UF₃, the specimens melted in argon at 885°C and in hydrogen at 935°C. This low melting point was unexpected in view of a reported* melting point of UF₃ of approximately 1495°C. At any rate, the material is unattractive as an alternate fuel for UO₂.

*R. W. M. D'Eye and F. S. Martin (AERE), "The Barium Fluoride - Uranium Trifluoride System," *Journal Chemical Society*, 1957, Vol. No. 7, 1957, pp. 1847-1851.

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Uranium Mononitride

Uranium mononitride (UN) was investigated as an alternate fuel element on the basis of several advantages over UO_2 : higher melting point (2885°C compared to 2800°C), higher density (14.32 compared to 10.97 g/cm^3), lower coefficient of expansion (9.7×10^{-6} compared to $10.5 \times 10^{-6}/^\circ\text{C}$), and a higher fuel content per unit volume. For fuel element evaluations, Fe - 40UN compacts made with commercially produced UN were sintered in dry hydrogen at 1100°C to 72 percent of theoretical density. Cores were prepared for both capsule-type and die specimens and will be processed for stability testing at temperatures up to 1250°C early in CY-64.

FUEL ELEMENT CLADDING ALLOY DEVELOPMENT AND FABRICATION

The objectives of the alloy development work are to improve both the Fe-Cr-Al-base alloys and the Cr-base alloys for fuel element applications in oxidizing atmospheres of air or steam at temperatures in the range of 450° to 1300°C . The development of alloy systems resulting from earlier research on high-temperature oxidation resistant materials is being emphasized.

Fe-Base Alloys

The work on Fe-base alloys during CY-63 was concerned with modifications of the Fe-Cr-Al-Y alloys, to minimize low-temperature embrittlement and to increase strength and melting points. The production of thin-wall tubing was also initiated.

Melting Points - The Fe - 25Cr - 4Al - 1Y alloy exhibits a wide melting temperature range because of the presence of a low melting phase, YFe₃. The YFe₃ phase melts at about 1350°C , and the matrix at about 1450°C . The low melting temperature limits the application temperature and is basically detrimental to weldability. A number of rare-earth elements which form stable oxides were evaluated as substitutes for Y in the alloy. The elements Nd, Gd, Dy, Yb, and Er all combined with iron to form phases with melting temperatures equal to, or less than that of Y, and no temperature advantage would be gained by substituting them for Y in the alloy.

Alloy Modifications - To determine the effects of low and intermediate temperatures on the structural stability and oxidation resistance of the Fe-Cr-Al system, a series of Fe-base alloys was evaluated. The nominal compositions of the alloys are shown in Table 2.2-3. The purpose of this evaluation is threefold: (1) to demonstrate the effects of Cr, Al, and Y contents on the structural stability, (2) to evaluate substitutes for Y, such as Sm, Th, Be, and Mischmetal, and (3) to determine the effect of Nb on high-temperature strength.

TABLE 2.2-3
NOMINAL COMPOSITIONS OF
EXPERIMENTAL Fe-Cr-BASE ALLOYS

Heat No.	Nominal Composition, wt. %
M-229	Fe - 25Cr (Standard)
MS-8	Fe - 25Cr - 1Y
M-232	Fe - 25Cr - 4Al (Base Alloy)
M-228	Fe - 25Cr - 4Al - 1Y
M-223	Fe - 25Cr - 4Al - 1Sm
M-185	Fe - 25Cr - 4Al - 1Th
M-233	Fe - 25Cr - 4Al - 1Nb - 1Y
M-227	Fe - 25Cr - 4Al - 1Mischmetal
M-226	Fe - 25Cr - 4Al - 0.1Be - 0.2Y
M-230	Fe - 15Cr - 4Al
M-231	Fe - 15Cr - 4Al - 1Y

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Evaluation of the alloys is not yet completed; however, initial data show that some of the alloys tend to become embrittled at low temperatures. The bend test results after 1000 hours at 450°C are shown in Table 2.2-4. The results were substantially the same after only 100 hours, indicating that the embrittling factor was a relatively short-time reaction. Except for the binary Fe - 25Cr alloy, all the alloys containing 25 percent Cr became embrittled. The alloys which contained 15 percent Cr were less susceptible to embrittlement. The Fe - 15Cr - 4Al - 1Y alloy (Heat No. M-231) was tested in the annealed condition and found to be ductile after 100 hours at 450°C. All alloys were ductile after testing at 650°, 750°, 900°, 1100°, and 1300°C unless they failed from prior oxidation.

TABLE 2.2-4
RESULTS OF BEND TESTS SHOWING EMBRITTLEMENT OF Fe-Cr-BASE
ALLOYS AFTER 1000 HOURS AT 450°C IN AIR

Heat No.	Nominal Composition, wt %	Condition ^a	Bend Test Results ^b	
			Before	After
M-226	Fe - 25Cr - 4Al - 0.1Be - 0.2Y	Annealed	Ductile	Brittle
		Cold-Rolled	Ductile	Brittle
M-228	Fe - 25Cr - 4Al - 1Y	Annealed	Ductile	Brittle
		Cold-Rolled	Brittle	Brittle
M-229	Fe - 25Cr	Annealed	Ductile	Ductile
		Cold-Rolled	Ductile	Ductile
M-230	Fe - 15Cr - 4Al	Annealed	Ductile	Ductile
		Cold-Rolled	Ductile ^c	Ductile
M-231	Fe - 15Cr - 4Al - 1Y	Cold-Rolled	Brittle	Brittle
M-232	Fe - 25Cr - 4Al	Cold-Rolled	Ductile	Brittle

^aAnnealed at 1000°C for 1 hour or cold-rolled, approximately 50% reduction.

^bDuctile: 90-degree bend over a knife edge at room temperature;

Brittle: less than 10-degree bend over a knife edge at room temperature.

^cDuctile only to 45-degree bend.

In a study of short-time aging behavior, six alloys representing basic compositional variations were annealed at 1000°C, water-quenched, and aged at 370° to 650°C. The hardness of the rod specimens was measured periodically. The results for the most critical temperature, 450°C, are shown in Figure 2.2-0. The alloys containing only 15 percent Cr were relatively stable. A comparison of the Fe - 25Cr - 4Al alloy with a similar alloy containing Y, indicated that Y increased the rate of hardening at 450°C. The alloys containing 25 percent Cr also exhibited double aging peaks at 550°C, probably a result of solutioning and re-aging. The data indicate that the aging behavior of the alloys is similar to that of the basic Fe-Cr binary alloy system.

The low-temperature portion of the Fe-Cr equilibrium diagram, as shown in Figure 2.2-7, shows that at temperatures below 520°C a Cr-rich ferrite (α') precipitates in the Fe-rich ferrite matrix (α).^{*} To determine if the hardening is caused by α' precipitation or by normal age-hardening, the various Fe-Cr-base alloys were first aged at 450°C, softened at 650°C for 1 hour, then re-aged at 450°C. The results are shown in Figure 2.2-8. The alloys hardened upon re-aging at 450°C, indicating that the hardening was caused by α' precipitation; α' , being a very small, coherent precipitate, was readily dissolved upon heating to 650°C; it therefore would precipitate again when the alloys were re-aged at 450°C. If the hardening were due to precipitation of YFe₃, the alloys would not harden to the same extent during re-aging.

^{*}R. O. Williams, "Further Studies of the Iron-Chromium System," GERL57-RL-1730, April 1957.

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Fig. 2.2-6— Hardness of various Fe-Cr-base alloys as a function of aging time at 450°C

Fig. 2.2-7— Low-temperature portion of Fe-Cr phase diagram

The 15-percent Cr alloys exhibited much less hardening than the 25-percent Cr alloys, indicating that for service at temperatures below 520°C, the Cr content should be less than 15 weight percent. The Fe-Cr phase diagram indicates that sigma phase precipitation will occur after long times in the temperature range of 550° to 650°C; for this reason, also, the Cr content must be reduced.

Oxidation Resistance - Oxidation resistance comparable to the Fe - 25Cr - 4Al - 1Y alloy was shown by the following alloys: Fe - 15Cr - 4Al - 1Y (Heat M-231), Fe - 25Cr - 4Al - 1Nb - 1Y (Heat M-233), Fe - 25Cr - 4Al - 1Th (Heat M-185), and Fe - 25Cr - 4Al - 1Sm (Heat M-223). The alloys containing Sm exhibited a low weight gain, but a lateral

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Fig. 2.2-8 - Effect of over-aging treatment on the aging behavior of various Fe-Cr-base alloys at 450°C

growth of about 20 percent occurred in 1000 hours at 1300°C. This growth phenomenon was not observed in the other alloys. The appearance of six of the alloys after testing for 100 hours in air at 900°, 1100°, and 1300°C is shown in Figure 2.2-9; the effects of Al and Y on the oxidation behavior of these six specimens are clearly demonstrated by their appearance.

The alloy which contained only 15 percent Cr is of primary interest because of its improved stability at low temperatures as discussed under "Alloy Modifications." The weight gain rate for the 15-percent Cr alloy at 1100°C and 1300°C is shown in comparison with the 25-percent Cr alloy in Figure 2.2-10. The alloys are essentially equal in oxidation resistance.

Tubing Fabrication - A procedure was developed for production of small quantities of Fe-Cr-Al-Y alloy tubing. Tube blanks were prepared by extruding the alloy at 1000°C over a mandrel. The resultant tube blank (1.6 cm ID, 2.8 cm OD, 214 cm long) was cut to lengths of 30.5 centimeters. These blanks were machined to 1.9 centimeters ID and 2.54 centimeters OD prior to drawing. Two such blanks were supplied to a commercial producer for drawing to finished tubing. One blank was successfully drawn at 370°C to 1.43-centimeter-diameter tubing having a wall thickness of 0.76 millimeter. The other blank fractured during processing, apparently from the presence of oxide stringers in the tube blank. The stringers, identified by microprobe analysis to be rich in Y and Al, were formed either during the melting and casting of the alloy or during extrusion. This defect was not noted in other heats of the same alloy. Additional heats of both the 15- and 25-percent Cr alloys were prepared and will be extruded for additional tube blanks.

Cr-Base Alloys

The advantages of Cr-base alloys over Fe-base alloys for fuel element applications include greater strength and inherently better oxidation resistance. The primary problem areas are lack of low-temperature ductility and susceptibility to nitriding when heated in air.

The addition of Re to Cr improves the low-temperature ductility. Alloys containing 65 to 70 percent Re exhibit good ductility in the recrystallized condition at temperatures well below room temperature. Because of its similarity to Re, Ru was investigated as a substitute for Re. A powder metallurgy alloy having a composition Cr - 20Ru (at.%) was press-forged and rolled with intermediate anneals to 0.5-millimeter-thick strip. Both transverse and longitudinal samples of this strip could be bent 30 to 90 degrees. This discovery led to a further examination of other ductilizers for Cr based on a proposed theory to explain the effects of Re and Ru. The proposed theory was based on four factors: valence, intermediate

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Heat No.	GE-NMPO		
M-226			Fe - 25Cr - 4Al - 0.2Y - 0.1Be
M-228			Fe - 25Cr - 4Al - 1Y
M-229			Fe - 25Cr
M-230			Fe - 15Cr - 4Al
M-231			Fe - 15Cr - 4Al - 1Y
M-232			Fe - 25Cr - 4Al
	900°C	1100°C	1300°C

Fig. 2.2-9 - Annealed Fe-Cr-base alloys, 0.76 mm thick, oxidized for 100 hours in air at 900°, 1100°, and 1300°C (Negs. P63-10-5G, H, D)

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Fig. 2.2-10—Weight gain as a function of time for two Fe-Cr-Al-Y alloys tested at 1100°C and 1300°C in static air

sigma phase, hexagonal-close-packed structures, and the solute solubility. These four factors are discussed below.

The valence of the solute is important for two reasons. The addition of a solute exhibiting a valence greater than +6 apparently increases the tolerance of Cr for interstitial impurities, such as O, N, and H₂. Increasing the electron-to-atom ratio in this manner may either increase or decrease the interstitial solubility. The Group VI-A metals, Cr, Mo, and W, exhibit a low tolerance for interstitial impurities. In either case, it was noted that Re and Ru tend to reduce the grain boundary oxide concentrations usually found in Cr. Assuming that a valence of greater than +6 is a necessary requirement for a potential ductilizer, the metals of Groups VII and VIII which satisfy this requirement are listed in Table 2.2-5. Another effect which may be attributed in part to the valence of the solute is the type of intermediate phase which is formed in the alloy system.

TABLE 2.2-5
COMPARISON OF SOLID SOLUTION ADDITIONS AS POTENTIAL DUCTILIZERS
FOR CHROMIUM

Groups VII and VIII Metals (Valence >+6)	Intermediate Sigma Phase	Hexagonal- Close-Packed Phase In System	High Solubility In Cr	Potential Ductilizer
Mn	Yes	No	Yes	No
Fe	Yes	No	Yes	No
Co	Yes	Yes	Yes ^a	Yes
Ni	No	No	Yes ^a	No
Tc	Yes	Yes	Unknown	Yes
Ru	Yes	Yes	Yes	Yes
Rh	No	Yes	No	No
Pd	No	No	No	No
Re	Yes	Yes	Yes	Yes
Os	Yes	Yes	Moderate	Yes
Ir	No	Yes	No	No
Pt	No	No	No	No

^aSolubility of these elements is limited at low temperatures, but increases at higher temperatures.

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The second factor which appears to be important is that sigma phase, which is a body-centered-tetragonal structure, forms in the alloy system. All the known systems which exhibit improved ductility (Cr-Re, Cr-Ru, Mo-Re, and W-Re) contain this phase. Sigma phase forms very slowly, at least in annealed structures, thus permitting supersaturation of the matrix with respect to the solute. Under such a condition, the solute may segregate and form solute-rich zones, particularly at defect surfaces. Furthermore, it is possible that the solute-rich clusters tend to exhibit the structure of the solute.

All known ductilizers are of the hexagonal-close-packed (HCP) structure, the third factor. Initially, the ductile alloys, Cr-Re, Cr-Ru, Mo-Re, and W-Re, deform by twinning at low temperatures. This indicates that the initial stress for twinning is lower than that for slip or cleavage. Since some HCP metals exhibit considerable deformation twinning, possibly because of low stacking fault energies, it seems possible that, in the ductile alloys, twin nuclei are formed in the HCP zones. Possible interactions between HCP zones and dislocations can result in the formation of twin nuclei through decreased stacking fault energies. The critical stresses for twinning are thus lowered, permitting relatively easy initial deformation by twinning.

The solute should be moderately soluble in Cr to permit a high degree of supersaturation of the matrix. The solubility per se is probably less important than the slope of the curve for terminal solubility versus temperature. The lower the slope, the greater the degree of supersaturation and the better the ductility. Chromium-ruthenium alloys are particularly good examples of this. The solubility of Ru in Cr is greater than 45 percent at 1500°C, but only about 33 percent at 1000°C.

Most of the solutes listed in Table 2.2-5 were found to conform to the ductilizing theory. Additional studies, discussed below, of the Cr-Ru and Cr-Co systems were completed and provide good support for the above postulates.

Cr-Ru Alloys - The optimum Ru content in Cr was found to be 20 atomic percent (33 wt %) which is the solubility limit at 1000°C. Thin sections of alloys containing 20 to 35 atomic percent Ru could be readily cold-rolled from the as-cast condition to 50-percent reductions or more. Ingots weighing 80 grams were arc-melted and drop-cast into either cylindrical or rectangular copper chill molds. The ingots were hot-worked at 1000°C in air then cold-worked in approximately 90-percent reductions to finished dimensions.

Bend tests were performed on sheet specimens of the Cr - 20Ru alloy as-rolled and after annealing at 900°, 1100°, 1300°, and 1500°C. The results are shown in Table 2.2-6. Some of the embrittlement noted after annealing is due to contamination during annealing.

TABLE 2.2-6
EFFECT OF HEAT TREATMENT ON BRITTLE-DUCTILE
TRANSITION TEMPERATURE OF Cr - 20Ru ALLOY

Treatment	Bend Transition Temperature, ^a °C	Impurities, ^b ppm	
		O ₂	N ₂
As cold-rolled (~80% reduction)	<-196	152	8
1 hr at 900°C in H ₂	<-78, >-196	149	26
1 hr at 1100°C in H ₂	<25, >0	129	120
1 hr at 1300°C in H ₂	>25	40	106
1 hr at 1500°C in H ₂	>25	46	59
1 hr at 1300°C in H ₂ ^c	<25	-	-

^aSheet specimens (0.38-mm thick) bent 90 degrees over a 1.5-mm radius.

^bVacuum fusion analyses.

^cTa gettered.

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Another factor may be the grain growth which occurs during high-temperature annealing. The recrystallization temperature of the alloy was determined to be approximately 900°C. It thus appears that the alloy is more ductile in the cold-worked than in the annealed condition.

Cr-Co Alloys - Further confirmation of the ductilizing theory was obtained from a study of Cr-Co alloys. The solid solubility of Co in Cr is only about 10 atomic percent at 900°C, but increases to about 35 atomic percent at 1260°C.* The postulated theory indicates that supersaturation of the solute is a necessary condition. Accordingly, alloys containing 10 to 40 atomic percent Co were prepared by drop-casting arc-melted buttons into a Cu chill mold. The alloys appeared to be single phase up to 35 atomic percent Co where a slight amount of second phase, presumably sigma phase, was formed. Sections, 2.5 millimeters thick, were cut from the castings and cold-rolled in 50-percent reductions. Considerable ductility was experienced in cold-rolling all compositions, but the optimum workability occurred for the alloy with 30 atomic percent Co which showed little cracking. With a Co content as low as 18 atomic percent, extensive deformation twinning occurred. The cracking which occurred appeared to be initiated at grain boundaries, and in some cases at twin intersections. The hardness of the Cr-Co alloys averages about 600 DPH which is about 5 times the hardness of pure Cr.

The ductilizing theory remains a postulate since solute segregation or clustering was not proved. Further, the mechanics by which solute segregation resulted in easy twinning were even less easily visualized. However, the empirical correlations obtained indicated promising areas for further study.

Mechanism of Deformation in Cr-Base Alloys - A research investigation of the effect of alloying on the mechanisms of deformation in Cr and its alloys was carried out at Battelle Memorial Institute under subcontract AT5-998. The primary objective of this work was to establish the nature of the dislocation arrangements that are generated in binary alloys containing Re and Fe.

In addition to unalloyed Cr, other alloys investigated were Cr - 5Re, Cr - 15Re, Cr - 25Re, Cr - 35Re, and Cr - 35Fe (at. %). Cylindrical specimens were machined from drop-castings, annealed, then deformed 6 percent in compression at room temperature, and 6 percent individually at -150°C at a strain rate of 0.5 percent per minute. After unloading, the specimens were aged for 1 hour at 200°C in an attempt to prevent the re-arrangement of dislocations during the preparation of thin foils. The specimens were cut into discs, 0.51-millimeter-thick on a plane 45 degrees to the longitudinal axis of the specimens. In preparing the electron-transparent foils, the centers of the discs were electrolytically indented by a jet of 10-percent HCl. The indentations were then electro-polished to the point of perforation in a solution of perchloric and acetic acids. Foils prepared in this manner are transparent to electrons in the vicinity of the perforations. The foils were then examined in the electron microscope to determine dislocation arrangements.

In unalloyed Cr, the dislocations were fairly uniformly distributed without cellular structure. The dislocations were not straight but contained many curves, cusps, and trails. The foils contained a large number of dislocation loops of various diameters up to 0.5 micron. The axis of these loops, projected into the plane of the foil, was always identified with a $\langle 111 \rangle$ direction, to within the experimental uncertainty. Also, columns of prismatic dislocation loops punched out along $\langle 111 \rangle$ directions by precipitate particles were frequently observed in these foils. It was noted that, as the interstitial impurity level was decreased, the quantity of dislocation loops decreased indicating a possible

*C. Hansen, *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958, p. 466.

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correlation between dislocation loops and ductility since the ductility usually is increased as the impurity level is decreased.

The dislocation arrangements in the Cr - 5Re (at. %) alloy were similar to those in unalloyed Cr. In alloys containing 15 or more atomic percent Re, the arrangement was clearly different; dislocations were distributed more uniformly and were predominantly straight. The straightness indicated an ease of dislocation movement and therefore improved ductility. The dislocation loops found in unalloyed Cr were not present to any great extent in the high-Re alloys.

The Cr - 35Fe alloy also exhibited straight dislocations to a degree even higher than the Cr - 35Re alloy. The ductility in compression of this alloy was apparently high but it was not determined in tension. The correlation between straight dislocations and improved ductility was therefore unconfirmed.

This work demonstrated that the addition of Re to Cr results in significant changes in dislocation arrangements which are apparently related to the improved ductility.

CLADDING EVALUATIONS IN STEAM

Because of its excellent oxidation resistance, the Fe - 25Cr - 4Al - 1Y alloy (designated 2541) should be useful as a cladding material in high-temperature steam reactors and superheated steam systems. Preliminary corrosion tests performed by GE-HAPO on samples of the Fe-Cr-Al-Y alloys in oxygenated steam for 100 days at 550°C and 200 kg/cm² pressure showed corrosion resistance comparable to the best commercial alloys. Because of this potential, work was initiated early in the year on steam corrosion testing at GE-NMPO. The objective of this work was to determine the steam corrosion resistance of advanced fuel element cladding alloys in comparison to selected commercial alloys currently being used in superheated reactors. The emphasis was placed on the 2541 alloy, the chromium-base alloys developed by GE-NMPO, and the 80Ni - 20Cr alloy.

A low-pressure test facility was constructed capable of testing coupon specimens at maximum steam temperatures up to 815°C. A schematic of this system is shown in Figure 2.2-11. Steam is produced from demineralized water in the boiler at saturation conditions of 3 atmospheres and 150°C. A booster using plant steam in a concentric double-tube coil maintains the working steam temperature to the superheater. Superheating is accomplished in an Inconel tube which is heated resistively to produce temperatures up to 730°C at the inlet to the test chamber. The steam passes through the test chamber at a velocity of 40 cm/sec; spent steam is condensed in a water-cooled coil and drained away. The system is constructed of Type-316 stainless steel. The 10-centimeter-diameter test chamber has a capacity of 24 coupon specimens. The thickness of the 2.5- by 5.1-centimeter specimens ranged from 0.51 to 2.5 millimeters.

A second system was constructed for testing in highly superheated steam at temperatures up to 1370°C. This system is shown schematically in Figure 2.2-12. The test chamber is an alumina or Inconel tube, 5 centimeters in diameter, mounted vertically in a tube furnace and connected to an external water reservoir and condenser loop. The system is closed to the atmosphere except for a pressure relief valve. A secondary recirculating loop is pressurized by a centrifugal pump to provide metered water to the lower tube section. Boiling and presuperheating to 815°C occurred in a bed of alumina. The steam temperature was measured in the furnace tube to the maximum of 1370°C in the high-temperature zone where the specimens were suspended. Steam velocity over the specimens was 80 cm/sec. The steam is then condensed and the water accumulated for recirculation.

Water chemistry is monitored in both systems by sampling the inlet and condensate water. Analyses are performed periodically for specific resistivity (Cl⁻), pH, and dissolved oxygen.

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Fig. 2.2-11—Schematic diagram of low-pressure superheat corrosion-test apparatus

Fig. 2.2-12—Schematic diagram of apparatus for corrosion testing of cladding alloys in steam at temperatures up to 1370°C

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Low-Temperature Testing

The initial test was conducted at 540°C, the superheated steam critical temperature. Since the fuel elements in service are expected to develop hot-spot temperatures as high as 730°C, the subsequent tests were conducted at 730°C. Sheet specimens of 2541 alloy, Nb-stabilized 80Ni - 20Cr, and Type-304 stainless steel (18Cr - 8Ni) were tested in the annealed condition with a vapor-blasted surface at 540°C for 409 hours. The weight gain data from this initial test did not permit any valid conclusion as to the relative merits of the three alloys, but it did confirm the previously reported findings that the 2541 alloy had excellent corrosion resistance to deoxygenated steam.

All further testing was conducted at conditions of 730°C and 3 atmospheres pressure with a flow rate of 7.5 kg/hr of water, equivalent to a steam velocity of 38.6 cm/sec over the specimens. The steam chemistry obtained from samples of the condensate taken periodically during a 1000-hour test averaged, for 15 samples, 0.9 megohm/cm specific resistance, 5.9 pH, and 1 to 3 ppm of oxygen. The tests were conducted in increments of 250 to 425 hours and the weight change was measured after each increment. The initial group of samples was tested for 2036 hours at the end of the year. The corrosion rates of the 2541 alloy, Nb-stabilized 80Ni - 20Cr, and Type-304 stainless steel are shown in Figure 2.2-13 with comparative data for both acid-pickled and vapor-blasted surface conditions.

Fig. 2.2-13—Corrosion rates of 2541 alloy, Nb-stabilized 80Ni-20Cr, and Type-304 SS in demineralized superheated steam at 730°C and 3 atmospheres

The Type-304 stainless steel specimens with pickled surfaces spalled during the initial test period with an attendant weight loss. The vapor-blasted specimens did not spall and showed a normal weight gain. The specimens of 2541 alloy and 80Ni - 20Cr alloy showed little difference in corrosion resistance between the vapor-blasted and the pickled-surface conditions after about 1200 hours of testing.

Specimens of each alloy were removed from test periodically for metallographic examination. The typical corrosion of each of the alloys tested in the pickled condition at 730°C is shown in the photomicrographs of Figure 2.2-14. After 328 hours the specimen of Type-304 stainless steel showed scaling and internal oxidation, with cracking and spalling of the oxide layer. The 80Ni - 20Cr alloy showed scaling and mild internal oxidation after 1000 hours, whereas the 2541 alloy showed only a thin oxide formation with

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Fig. 2.2-14—Steam corrosion of surfaces of three alloys tested at 730°C in steam generated from demineralized water. All specimens were tested in the annealed and pickled condition.

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some surface roughness, which was attributed to initial pickling, after 1000 hours. No significant loss in thickness occurred in either the 2541 alloy or the 80Ni - 20Cr alloy, but the Type-304 stainless steel specimens lost as much as 0.13 millimeter in thickness after 1000 hours at 730°C, and the oxide layer measured 0.06 millimeter.

Other alloys were included in the 730°C series of tests. To provide standards for comparison, commercial alloys Incoloy 800, Inconel 600, and Hastelloy X were tested, together with the experimental GE-NMPO alloy 1541 (Fe - 15Cr - 4Al - 1Y). These materials had been tested for 757 hours by the end of CY-1963. The 1541 alloy showed corrosion resistance comparable to 80Ni - 20Cr alloy during the initial test period. The corrosion rates of the commercial alloys were about 6 times the rate for the 2541 alloy. These alloys are continuing on test to determine the overall corrosion resistance for long-time service.

High-Temperature Steam Corrosion Testing

High-temperature tests of metals and alloys for potential use in advanced-design, closed-cycle, steam-cooled power plants were initiated. The facility (Figure 2.2-12) was so designed that specimens could be evaluated in highly superheated steam with either recirculating (closed-cycle) or once-through (open-cycle) steam. Provision was also made for introducing helium or hydrogen to attain reducing conditions with respect to free oxygen in the steam. A water flow rate of 150 cm³/hr was used.

The materials tested at 1150°C or 1260°C were the experimental Cr - 20Ru (at. %) alloy, discussed previously under "Cr-Base Alloys," the 2541 alloy, the Nb-modified 80Ni - 20Cr alloy, and three commercial alloys. The test environment included combinations of hydrogen and helium mixed with the steam. Demineralized water was used and the condensate analyses showed pH values of 3.7 to 6.9 and specific resistances ranging from 0.001 to 0.11 megohm-cm. The oxygen content averaged 4 ppm for open-cycle operation and 2.02 ppm when hydrogen was introduced.

Weight gain data shown in Table 2.2-7 indicates that the Cr - 20Ru alloy is much less resistant to steam under these conditions than the 2541 alloy or 80Ni - 20Cr alloy. The addition of hydrogen was not effective in reducing the corrosion of either the Cr-Ru alloy or the 80Ni - 20Cr alloy. The 2541 alloy gained weight at 1260°C at about the same rate as in oxidation tests in air.

Cooperative Testing at GE-HAPO - As previously mentioned, the preliminary tests of the Fe-Cr-Al-Y alloys conducted in the high-pressure autoclave facilities at GE-HAPO

TABLE 2.2-7
CORROSION DATA FOR 2541, 80Ni - 20Cr, AND Cr-Ru ALLOYS
TESTED IN STEAM AT 1150°C AND 1260°C

Material ^a	Steam Temperature, °C	Maximum Test Time, hours	Average Weight Change In 100 Hours, mg/dm ²
2541 ^b	1150	1037	+45
2541 ^b	1260	328	+84
80Ni - 20Cr (Nb-Stabilized)	1150	158	-107 (spalled)
Cr - 20Ru (at. %)	1260	100	>2700 (spalled)
Inconel 702 ^c	1150	162	-135 (spalled)
Inconel 600 ^c	1150	145	+219
Incoloy 800 ^c	1150	328	+264

^aAll specimens were annealed and pickled. Specimen size 1.2 x 3.0 cm x 0.51 mm thick. Average weight 0.5 to 1.0 g.

^bFe - 25Cr - 4Al - 1Y.

^cTrade name, International Nickel Co.

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at 550°C demonstrated the potential of the 2541 alloy for superheated steam systems. These tests have been continued at GE-HAPO and broadened to include Nb-stabilized 80Ni - 20Cr alloy. Tests were conducted in steam generated from demineralized water at 550°C and 333 atmospheres pressure. The flow rate was 7.5 liters/hr and the oxygen content of the water was less than 0.1 ppm. Corrosion results after five cycles (1730 hours) are shown in Table 2.2-8. Type-304 stainless steel is included for comparison. The corrosion rates in high-pressure steam compare favorably with the data obtained at GE-NMPO in low-pressure steam.

TABLE 2.2-8
CORROSION DATA FOR CLADDING MATERIALS TESTED FOR 1730 HOURS
AT 550°C AND 333 ATMOSPHERES IN GE-HAPO AUTOCLAVE

Alloy	Surface Preparation	Average Weight Change In 100 Hours, mg/dm ²
Fe - 25Cr - 3Al - 0.5Y	Pickled	+3.3
80 Ni - 20Cr (Nb-Stabilized)	H ₂ Annealed	+2.9
Type-304 SS	Pickled	+8.3

It should be noted that the Fe-Cr-Al-Y alloy tested at GE-HAPO was not the standard 2541 alloy but was of an experimental composition with lower aluminum and yttrium contents. It was of the same family of alloys, however, and the results were promising. The 2541 alloy has since been supplied to GE-HAPO for autoclave testing.

Cooperative Testing at GE-APED - Arrangements were also made to test cladding materials in the superheat corrosion test facility (CL-1) at GE-APED. This facility simulates the steam flow and chemistry conditions in the Vallecitos Experimental Superheat Reactor (VESR).

Specimens of two heats of the 2541 alloy were tested in the CL-1 facility at 620°C and 69 atmospheres for 950 hours. The weight changes measured after descaling the specimens are shown in Table 2.2-9. Steam chemistry averaged 20 ppm dissolved oxygen, 2.5 ppm hydrogen, and less than 5 ppm chloride impurity. The weight losses shown for 2541 alloy are comparable to those of Inconel under the same conditions at lower temperatures (505°C).

TABLE 2.2-9
CORROSION DATA FOR 2541 ALLOY TESTED
UNDER SUPERHEAT REACTOR CONDITIONS^a

Surface Condition	Descaled Weight Loss, mg/dm ²	
	Heat MS-7	Heat MS-16
Pickled	30	52
Vapor-blasted	50	58

^aTest conditions: 620°C and 69 atmospheres;
duration: 950 hours.

SUMMARY AND CONCLUSIONS

The evaluations of fuel materials suitable for use with the oxidation-resistant Fe-Cr-Al-Y alloy (2541) were concerned primarily with UO₂ and US, with less emphasis on UF₃ and UN. For applications requiring fuel element temperatures of 1100° to 1250°C, UF₃ was found to be of no value because of its low melting point (935°C). Higher purity US was found

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to be readily reduced, allowing diffusion of uranium. Uranium nitride has not yet been tested. Uranium dioxide, dispersed in either a Cr or an Fe matrix and clad with Fe-Cr-Al-Y alloy, remained stable for at least 1200 hours at 1250°C in flowing air. The use of agglomerated UO₂ particles or ThO₂-stabilized UO₂ appeared to improve the fuel stability to some extent.

Modifications in the composition of the Fe-Cr-Al-Y alloy were studied to reduce the tendency toward embrittlement at low temperatures (450°C) and to improve the high-temperature strength. Embrittlement was attributed to hardening as a result of precipitation of a Cr-rich phase in the Fe-base matrix. A Cr content of 15 percent provided oxidation resistance equivalent to the 25-percent Cr alloy and this alloy was less susceptible to embrittlement. However, the 1-percent Y addition was found to be essential to stabilize the protective alumina film which provides the long-time oxidation resistance.

The fabrication of thin-wall tubing of Fe-Cr-Al-y alloy was accomplished by warm-drawing an extruded tube blank at 370°C. The initial tubing, 1.43 centimeters in diameter with a wall thickness of 0.76 millimeter, was found to have minor defects in the form of laps on inside surfaces.

A study of the effects of various additive elements on the ductility of Cr showed that both Ru and Co improved the ductility in much the same manner as Re additions. An alloy of Cr - 20Ru (at. %) was hot-worked (1000°C) from the arc-cast ingot and then cold-rolled to sheet and rod in 80- to 90-percent reductions at room temperature. The ductile-to-brittle transition temperature, as determined by bend ductility, lies below -196°C in the cold-rolled condition and below -78°C after recrystallization. Chromium-cobalt alloys containing 20 to 35 percent Co exhibit extensive twinning in the arc-cast structure. These alloys have been cold-rolled to sheet from the arc-cast structure and show good bend ductility at room temperature. Similar ductilizing effects on Cr have been found for many of the elements of Groups VII and VIII. It appears that the solute metal must be hexagonal in structure to improve the ductility of Cr.

Both the Fe - 25Cr - 4Al - 1Y (2541) and 80Ni - 20Cr alloys were found to be highly corrosion-resistant in low-pressure steam at 730°C for at least 2000 hours. These alloys were tested in comparison with conventional alloys at GE-NMPO in the temperature range from 500° to 1300°C, at GE-HAPO in high-pressure steam at 550°C, and at GE-APED under simulated superheat reactor conditions at 620°C. The 80Ni - 20Cr and 2541 alloys showed similar corrosion resistance, an improvement by a factor of 2.5 over Type-304 stainless steel at 550°C. At high temperatures (1150°-1260°C), the 2541 alloy showed resistance to steam corrosion comparable to its oxidation resistance in air. All tests were made in steam generated from demineralized water.

PLANS AND RECOMMENDATIONS

Evaluations of fuel materials will be continued; UO₂ and UN will be of primary interest. Fuel elements of the Fe-Cr-Al-Y-clad Fe-UO₂ system will be fabricated for laboratory evaluations under thermal cycle conditions and for in-pile tests of fission product retention and irradiation stability. In parallel, work will also be continued on the potentially higher temperature Cr-UO₂ core system.

To establish the optimum composition for the Fe-Cr-Al-Y alloy, the development of fuel element cladding materials will be concerned with effects of the Cr-Al ratio on structural stability and oxidation resistance. Both the 2541 alloy and the new 1541 alloy will be evaluated, and increased efforts will be applied to the fabrication of thin-wall tubing of both alloys. A compilation of physical and mechanical properties of the Fe-Cr-Al-Y alloys will be made. Solid solution additions and stable oxide dispersions will be evaluated in an effort to improve the strength of these alloys. Oxidation data will be obtained from high-temperature air tests for times up to 10,000 hours.

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Iron-base alloys developed under this program will be evaluated in low-pressure steam over a range of temperatures, with emphasis on long-time simulated-service corrosion testing at superheat temperatures (550°-730°C). In-pile tests of fueled rods fabricated of Fe-Cr-Al-Y tubing in a steam environment are planned. The effects of chloride ions on the corrosion resistance of these alloys will be studied in boiling water (550°C and 70 kg/cm²) reactor systems.

2.3 GRAPHITE FUEL ELEMENT MATERIALS RESEARCH (57013)

The purpose of this program is to obtain scientific information and engineering data for improving the processing, reliability, and service capabilities of graphite fuel elements.

Graphite has greater strength at higher temperatures than most known materials, has excellent resistance to thermal shock, is lightweight, and is easily machined. These attributes have focused much attention on the possibility of high-temperature nuclear fuel elements using graphite as the base material. Maximum utilization of these high-temperature properties for nuclear application necessitates the development of a new uranium-bearing fuel. In addition to studies on new fuel-bearing materials, work was undertaken to evaluate various organic resins as graphite binders and to synthesize organic compounds of known structures that would carburize on pyrolysis without excessive gaseous evolution, leaving a high percentage of graphitizable carbon.

COMPLEX CARBIDE FUELS

The work on this phase of the program was a continuation of previous work* on the development of nuclear fuels for use in high-temperature graphite fuel elements. Most of the effort was devoted to research on complex carbides as fuel additives. Of the many known carbides, only the complex carbides of ZrC-UC and NbC-UC were studied extensively. The criteria for the selection of these carbides were based on their inherent low thermal neutron cross section, coupled with their low vapor pressure and high melting point. The effect on reactivity of varying the uranium-to-zirconium or uranium-to-niobium ratio of each complex carbide in a graphite matrix as a function of temperature was the principal point of interest.

(Zr, U)C Fuels

Following the evaluation of the reactivity of the 52 weight percent uranium, (Zr, U)C complex carbide in graphite as a function of temperature, during CY-62† efforts were directed toward a similar investigation on material containing 28.5 weight percent uranium.

Complex carbide fuels were prepared by the reactive sintering techniques previously described† and mixed into a graphite blend in an amount calculated to produce a fuel loading of 100 mg U/cm³. These blends were then graphitized at various temperatures. Fuel reactivity in graphite as a function of temperature was studied, using electron microprobe techniques to determine the nature of any compositional changes. The extremely small sizes of many of the fuel particles made it difficult to obtain absolute analytical values. Although the electron beam, per se, is about 1 micron in diameter, the resultant X-ray image that is counted is about 3 microns in diameter and any analysis of fuel particles less than 3 microns in diameter must also include a portion of the matrix. In interpreting the microprobe data on small particles, the relative amounts of uranium and zirconium are considered to be significant as a measure of fuel reactivity.

*"Second Annual Report - High-Temperature Materials and Reactor Component Development Programs, Volume II - Materials," GE-NMPO, GEMP-177B, February 28, 1963, pp. 209-232.

†Ibid., pp. 209-210.

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Figure 2.3-1 shows the change in chemical composition of fuel particles by microprobe analyses on three fuel particles in a graphite matrix which had been graphitized for 1 hour at 2600°C in argon. Particles within the graphite matrix appeared to range in composition from essentially pure ZrC to pure UC₂ with numerous (Zr, U)C solid solutions of varying uranium content. The microprobe data show that the 28.2 weight percent uranium (Zr, U)C fuel is not fully stable in graphite when exposed for 1 hour at 2600°C.

Fig. 2.3-1 - Electron microprobe traces showing the change in (Zr,U)C (28.5 wt % U) composition in graphite where graphitized at 2600°C

Microscopic examination showed the fuel particles in extrusions graphitized at 2200°C and 2400°C to be single phase. Static probe analyses on 8- to 50-micron diameter fuel particles in extrusions graphitized at 2200°C showed a uranium content varying from 15 to 23 weight percent. Zirconium concentration in these particles was found to vary from 62 to 71 weight percent. Although these analyses reflect the ranges in uranium and zirconium contents, analyses showed that most fuel particles were about 22 weight percent uranium and 62 weight percent zirconium, indicating that the average uranium content in the fuel particles decreased from the 28.6 weight percent uranium composition initially used. Microprobe traces across fuel particles and into the graphite matrix were made to establish the course of compositional changes in the fuel particles noted in this series of experiments. Figure 2.3-2 is a typical trace of a microprobe scan on fuel particles after graphitization for 1 hour at 2200°C. This scan over an 11- and a 30-micron fuel particle is typical of most of the particles in the body and indicates a uranium content of about 20 weight percent.

Electron microprobe techniques were also used to study changes occurring in fuel particles after graphitization for 1 hour at 2400°C. In general, the composition of particles in the graphite matrix ranged from 15 to 19 weight percent uranium and 66 to 70 weight percent zirconium. Static probes of individual fuel particles in the graphite matrix

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Fig. 2.3-2—Electron microprobe trace of two (Zr,U)C fuel particles in fueled extrusion graphitized at 2200°C for 1 hour

showed the larger fuel particles (50 to 90 microns) to be richer in uranium and slightly higher in zirconium content, while the small fuel particles (6 to 40 microns) exhibited lower uranium and zirconium contents. The majority of the fuel particles had a uranium content of about 20 weight percent, slightly lower than that of the fuel particles graphitized at 2200°C. Submicron-size, zirconium-depleted fuel particles were also detected. Chemical analyses of the graphitized fuel samples used in these tests showed that no uranium was lost from the initial loading; consequently, changes in the initial composition in the fuel particle must be the result of uranium migration into the adjacent graphite matrix.

Based on the foregoing analyses, and after evaluating metallographic, X-ray diffraction, hydrolysis (see Table 2.3-1), and electron microprobe data, the maximum graphitizing temperature was established at 2200°C for samples containing 28.5 weight percent (Zr, U)C fuel. Specific consideration was given to the X-ray diffraction data which indicated there was no UC₂ in the sample treated at 2200°C while a trace amount was detected in a specimen treated at 2400°C.

(Zr, U)C Fuels Containing 20.2 Weight Percent Uranium

The studies on the 28.2 weight percent uranium concentration in (Zr, U)C indicated that the uranium appeared to stabilize at approximately 20 weight percent. Because of this, studies were carried out to determine if the lower uranium composition exhibited greater stability in a graphite matrix. Fueled samples were prepared by extruding a graphite composition containing (Zr,U)C having 20.2 weight percent uranium. The samples were graphitized for 1 hour at 2400°, 2600°, and 2800°C. Data on these samples are given in Table 2.3-1.

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TABLE 2.3-1

STABILITY OF (Zr, U)C IN EXTRUSIONS AFTER GRAPHITIZATION AT VARIOUS TEMPERATURES

Uranium Content Of (Zr, U)C Fuel, wt %	Extrusion Number	Graphitization Temperature, °C	Post-Graphitization		Post-Graphitization Exposure To Water-Saturated Air ^c			
			Percent Of Theoretical Density	Micrographic Observations	Chemical Analyses		Fuel Loading, Mg U/cm ^{3d}	Weight Gain, %
					Weight Percent U	Weight Percent Zr		
28.5 ^a	A	2200	81.4	Poor fuel-matrix contact. No network-type second phase in fuel.	5.31	11.90	112	0.0143
	B	2400	82.1	Poor fuel-matrix contact. No network-type second phase in fuel.	5.29	12.00	112	0.0363
	C	2600	81.7	Good fuel-matrix contact. Fuel appears to be single phase. Fuel particles have been reduced to very small size.	5.38	11.98	113	0.0975
20.2 ^b	D	2400	80.2	No network-type second phase in fuel. Particle size of fuel unchanged.	4.77	16.18	103	0.0850
	E	2600	79.8	Approximately 50% of fuel has been converted to extremely small particles. Fuel particles which remain unchanged in size appear to be single phase and densified.	4.71	16.26	101	0.0963
	F	2800	79.3	Fuel particles reduced in size. Reaction appears to have occurred in matrix immediately surrounding fuel particles.	4.91	16.17	105	0.0964

^a(Zr, U)C fuel blend No. 28.5-40-RW, -200/+400 mesh, Tyler series.^b(Zr, U)C fuel blend No. 20.2-45-RW, -200/+400 mesh, Tyler series.^cExposed to water-saturated air at room temperature for 120 hours.^dCalculated 100 mg U/cm³ fuel loading

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Microscopic examination of the fuel graphitized at 2400°C showed no network-type second phase in the particles and the fuel size remained unchanged. Fuel in extrusions graphitized at 2600°C appeared to be single phase; however, about 50 percent of the fuel had converted to very small particles, apparently due to densification. All fuel particles in the extrusion graphitized at 2800°C changed to extremely small particles, and there was also a concurrent change in the graphite microstructure surrounding the fuel particle (Figure 2.3-3). Chemical analyses of the graphitized extrusions showed no change in total uranium content. Resistance to hydrolysis was measured by exposing samples to water-saturated air for 120 hours. The results shown in Table 2.3-1 reveal that the resistance to hydrolysis decreased with increasing graphitization temperature, although weight gains for samples graphitized at 2600°C and 2800°C are practically identical. The densities of these samples also decreased with increased graphitization temperatures. Attempts were made to determine the composition of fuel graphitized at 2800°C for 1 hour by electron microprobe analyses. The extremely small particle size of the fuel made interpretation of the electron microprobe analyses difficult. Numerous static microprobes were made on particles of 1 micron or less, and microprobe traces were made on particles as large as 8 microns. In general, the electron microprobe data (both static probes and traces) showed that compositional changes began to occur in fuel in a graphite matrix after graphitization at 2600°C, and that some particles are essentially ZrC, other particles are essentially UC₂, and numerous particles are solid solutions of (Zr, U)C, containing varying amounts of uranium.

Fig. 2.3-3—Photomicrograph of fueled graphite extrusion graphitized at 2800°C showing reduction in (Zr,U)C (20.2 wt % U) fuel particle size

Based on these data, the 20.2 weight percent uranium (Zr, U)C fuel was found to exhibit complete stability after graphitizing for 1 hour at 2400°C. When the graphitization temperature was increased to 2600°C, the fuel particles appeared to follow the pattern noted in the 28.5 weight percent fuel after graphitizing at 2400°C. Consequently, it appears that by reducing the uranium concentration in the (Zr, U)C composition, a graphitizing temperature approximately 200°C higher can be used for preparing fuel-graphite samples.

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(Nb, U)C Fuels

Concurrently with the studies on (Zr, U)C, work was performed to establish the degree of stability of (Nb, U)C fuels in a graphite matrix. (Nb, U)C samples containing 28.2 and 19.9 weight percent uranium were prepared by the double reaction sintering method.*† Extrusions fueled to a loading of about 100 mg U/cm³ were used to accumulate data, Table 2.3-2, on fuel stability of complex carbides on graphitizing at 2200°, 2400°, 2600°, and 2800°C. Chemical analyses of the graphitized extrusions indicated no major loss in total uranium content. Resistance to hydrolysis by water-saturated air, after 120 hours exposure, showed a small decrease with increasing graphitization temperature.

TABLE 2.3-2
STABILITY OF (Nb, U)C IN EXTRUSIONS AFTER GRAPHITIZATION AT VARIOUS TEMPERATURES

Uranium Content Of (Nb, U)C Fuel, wt %	Extrusion Number	Graphitization Temperature, °C	Percent Of Theoretical Density	Post-Graphitization Micrographic Observations	Post-Graphitization Exposure To Water-Saturated Air ^c			
					Chemical Analyses		Fuel Loading, mg U/cm ^{3d}	Weight Gain, %
					Weight Percent U	Nb		
28.2 ^a	A	2200	84.5	Good fuel-matrix contact. Second-phase platelets in fuel.	5.09	11.57	112	0.0252
	B	2400	85.2	Good fuel-matrix contact. Increase in number and size of second-phase platelets in fuel compared to 249-1-E1.	5.08	11.55	113	0.0572
	C	2600	84.1	Fuel-matrix contact not as uniform as in 249-1-E1 and E2. Increase in number and size of second-phase platelets in fuel compared to 249-1-E2.	4.97	11.35	109	0.1547
19.9 ^b	D	2200	83.8	Single-phase fuel. No second-phase platelets.	4.57	16.00	104	0.0159
	E	2400	83.9	Good fuel-matrix contact; single-phase fuel. Occasional second-phase platelets.	4.58	15.92	105	0.0482
	F	2600	84.1	Good fuel-matrix contact but matrix is cracked. Some fuel reduced to small particle size single-phase fuel. Occasional second-phase platelets.	4.50	16.67	103	0.0617
	G	2800	84.1	Reaction appears to have occurred in fuel-matrix contact area. Fuel appears single phase. Increased number of small fuel particles. Occasional second-phase platelets.	4.37	15.84	100	0.1386

^a(Nb, U)C fuel blend No. 28.2-42-RW, -200/+400 mesh, Tyler series.

^b(Nb, U)C fuel blend No. 19.9-46-RW, -200/+400 mesh, Tyler series.

^cExposed to water-saturated air at room temperature for 120 hours.

^dCalculated 100 mg U/cm³ fuel loading.

Figure 2.3-4 is a photomicrograph of a specimen containing 28.2 weight percent uranium graphitized at 2200°C. No coating developed by moisture reactivity on the (Nb, U)C fuel particles during the carbonizing cycle as had been noted on (Zr, U)C fuels, and there was excellent fuel - matrix contact after graphitization. A second phase (identified as platelets) can be seen within the fuel particles. Electron microprobe studies were made to determine the nature of the second-phase platelets within the (Nb, U)C fuel particles. The platelets could not be identified directly from the data; however, considering the limitations imposed by the relative size of the small platelets and the full X-ray image required for a total analysis, the platelets appear to be graphite.

*Ibid.

†"High-Temperature Materials Program Progress Report No. 13, Part B," GE-NMPO, GEMP-13B, July 31, 1962, pp. 47-49.

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Fig. 2.3-4 — Photomicrograph of fueled graphite matrix graphitized at 2200°C showing (Nb,U)C (28.2 wt % U) fuel particles

In contradistinction to the 28.2 weight percent uranium (Nb, U)C fuel treated at 2400°C, fuel particles containing 19.9 weight percent uranium were found to contain only an occasional platelet. Fueled extrusions treated at 2200°C and 2400°C tended to retain the original fuel particle size. Significant changes began to occur in the fuel samples after graphitization at 2600°C. At this temperature some of the fuel in the graphite matrix began to convert to very small particles. Many of the particles that retained their original size contained an occasional platelet; however, the amount of second phase was found to be less than that found in 28.2 weight percent uranium (Nb, U)C fuel treated at 2600°C.

A study made to determine the composition of both small and large fuel particles by electron microprobe analyses revealed no significant difference in composition between large and small particles. To obtain an overall evaluation of the compositions of most of the fuel particles, many static probes were made on particles too small to scan (some less than 1 micron in diameter); microprobe traces were made across the larger particles.

In summation of the static probe and microprobe trace data, many particles were found to be niobium-rich with only about 3 weight percent uranium. Many other particles were uranium-rich with uranium-to-niobium ratios as high as 5 to 1. No particles were detected which could be identified as UC_2 . This failure to detect UC_2 by microprobe analyses might reflect an insufficient sampling of the particles present in the matrix. The electron microprobe data are sufficiently reliable, however, to conclude that the 19.9 weight percent uranium (Nb, U)C fuel in a graphite matrix does not retain its original single-phase structure nor particle size after graphitization at 2800°C.

Zr-U Alloy Fuels

As a continuation of the effort to extend high-temperature fuel technology, a study on the preparation of complex carbides by solid-state carburization was undertaken. Solid-state, or in-situ, carburization requires that the fuel be initially prepared as a fuel alloy and comminuted to a powder of appropriate particle sizes prior to its incorporation into a

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graphite body. This study was based on the 20.2 weight percent uranium (Zr, U)C fuel that exhibits good high-temperature stability over a relatively wide range of graphitization temperatures.

Alloy Fuel Preparation - Initially, the Zr-U alloy was prepared by arc-melting metallic zirconium and uranium into 50-gram buttons. The limited amounts of fuel that could be prepared by this method necessitated the use of small warm-pressed specimens for carburization studies instead of extruded specimens. In order to continue research on extruded fuel specimens, it became necessary to process larger batches of fuel.

A recent batch of fuel was prepared by melting 1860 grams of zirconium and 540 grams of uranium in a vacuum melting induction furnace. The entire vacuum melting cycle was performed as rapidly as possible to minimize contamination. The melt produced a 1680-gram cylindrical casting of Zr - 22.5U alloy, measuring approximately 5.4 centimeters in diameter by 12.7 centimeters in length. The ingot was crushed, hydrided, comminuted to various particle size ranges, and the particles dehydrided. Photomicrographs showing the microstructure of the Zr-U alloy in various stages of processing are shown in Figure 2.3-5. X-ray and metallographic analyses are summarized in Table 2.3-3. These data indicate that a casting technique can be used to produce larger quantities of a uniform Zr-U alloy. Fuel produced by this method was used in the studies of spheroidization and of solid-state carburization in graphite matrices.

TABLE 2.3-3

SUMMARY OF X-RAY AND METALLOGRAPHIC ANALYSES OF INDUCTION-MELTED Zr-U ALLOY FUEL AT VARIOUS STAGES OF PROCESSING

Condition Of Fuel	X-Ray Diffraction Analysis	Metallographic Examination
After casting from 1950°C into cold copper mold	Major phase: alpha Zr Minor phase: delta UZr ₄ (approximate)	Eutectic microstructure, both phases appear metallic
After hydriding to 975°C and reduction to -200 mesh powder	Major phases: U and epsilon ZrH _x Trace phases: UO ₂ and delta ZrH _x	Non-metallic phase dispersed throughout metallic matrix. A third phase present in small amounts in matrix
After dehydriding at 850°C in vacuum and reduction to -100 mesh powder	Major phase: Zr with small amount of U in solution Minor phase: Delta UZr ₄ (approximate)	A metallic matrix containing a second metallic phase dispersed throughout the matrix

Spheroidization of Zr-U Alloy Fuel - Dehydrided Zr-U alloy particles generally had a wide size range including an excessive amount of fines, contained pores or large void areas, and were of diverse shapes. Spheroidization of these alloy particles in the high temperature of an argon plasma is a direct method to improve fuel density and uniformity of particle size. The spheroidizing experiments were conducted using a 4-megacycle induction unit (7.5 kw) to create an argon plasma. Argon was introduced at a rate of 12 to 14 liters per minute into the plasma generating apparatus. The fuel was spheroidized at a rate of 240 g/hr. The spheroidized fuel particles were collected in an argon-flooded vessel located at the exit end of the plasma tube. The particles formed are shown in Figure 2.3-6. As can be seen, a high percentage of all particles was spheroidized and all appear to be approximately the same size. Metallographic examination of the fuel revealed well-spheroidized, dense, fuel particles containing two metallic-appearing phases. X-ray diffraction analysis of this fuel indicated the presence of a major phase of zirconium and a minor phase of uranium. A minor phase, U-Zr₄, initially present in the feed material could not be detected in the spheroidized fuel.

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Neg. 3770

500 X

After casting from 1950°C
into cold copper mold

Neg. 3771

500 X

After hydriding to 975°C and
reduction to -200 mesh powder

Neg. 3772

500 X

After dehydriding at 850°C in vacuum
and reduction to -100 mesh powder

Fig. 2.3-5— Photomicrographs of Zr-22.5U (wt %) fuel at various stages of processing

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Neg. 3769

100 X

Neg. 3778

500 X

Fig. 2.3-6 - Photomicrographs of Zr-U fuel, VC-65, after spheroidization in an argon plasma

Solid-State Carburization Studies of the Zr-U Alloy in Graphite Matrices - Because the spheroidization studies and the solid-state carburization studies were run concurrently, sufficient quantities of spheroidized fuel were not available and, therefore, the carburization studies were made with unspheroidized fuel particles. To provide basic information on the possibility of using Zr-U alloys in future graphite extrusions, a series of warm-pressed graphite specimens containing Zr-U alloys was prepared with fuel loadings of 100 mg U/cm³. These fueled, warm-pressed graphite specimens were cured and carbonized to 850°C; they were then given in-situ carburization (or graphitizing) treatments for 1 hour at 2200°, 2400°, 2600°, and 2800°C in an argon atmosphere.

Results of X-ray diffraction and metallographic analyses of these fuel particles in graphite matrices after carburization are shown in Table 2.3-4. In summary, these data on the ZrU alloy fuel particles show:

1. No significant change in uranium content over the graphitizing temperature range of 2200° to 2800°C.
2. A single-phase solid solution fuel was attained in 1 hour at 2200°C.
3. Graphitizing for 1 hour at 2600°C resulted in a solid solution (Zr, U)C fuel and a small amount of UC₂.
4. Graphitizing for 1 hour at 2800°C resulted in a fuel of extremely fine particle size containing two solid solution (Zr, U)C phases but no UC₂.

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TABLE 2.3-4

SUMMARY OF X-RAY AND METALLOGRAPHIC ANALYSES OF Zr-U FUEL IN GRAPHITE MATRICES AFTER A 1-HOUR CARBURIZATION AT VARIOUS TEMPERATURES

Carburizing Temperature, °C	X-Ray Analyses	Metallographic Examination
2200	Single-phase solid solution (Zr, U)C containing ~26 wt % UC. No other phases detected	Most fuel particles single phase. Non-metallic phase in some particles. Fuel very porous
2400	Single-phase solid solution (Zr, U)C containing ~29 wt % UC. No other phases detected	Single-phase fuel, with large voids within fuel particles
2600	Solid solution (Zr, U)C containing ~26 wt % UC. Trace of UC ₂	Single-phase fuel, with large voids within fuel particles
2800	Two solid solution phases, a major phase of (Zr, U)C containing ~11 wt % UC and a minor phase containing about 32 wt % UC. No UC ₂ was detected	Fuel particles appear single-phase but underwent a great reduction in size

BINDER STUDIES

The objective of this work is to find a suitable organic material to use as a graphite binder. Graphite binders should undergo pyrolysis without excessive gaseous evolution and leave a high percentage of graphitizable residue.

A literature survey showed that over the past 30 years a considerable amount of work has been carried out in an attempt to develop an understanding of the mechanism of thermal degradation of organic materials.*†‡ In summary, this work has shown the mechanism of thermal degradation and the structure of the chemical entities that are products of thermal degradation and directly related to the molecular structure of the precursors. Work in the petroleum industry§ related to the cracking of hydrocarbons has shown that the tertiary carbon atoms in the chain weakens the adjacent c-c bonds. In this respect, the quaternary carbons are even more effective in weakening the adjacent c-c bonds. Organic compounds, having an abundance of hydrogen on the chain, form volatile products of varying molecular weight through random scission of the hydrocarbon chain during pyrolysis. A deficiency of hydrogen results in the formation of active sites and, perhaps, develops cross-linking between molecules; on prolonged heating the materials tend to stabilize. If the material is pyrolyzed, it will disproportionate to monomers or a carbonaceous residue.

Because cross-linkage appears to be an important mechanism for obtaining high carbon residues, the major area of the binder chemistry investigation is to develop a high degree of cross-linking in organic compounds. To establish the usefulness of different modes for inducing cross-linkage, both gamma and electron radiation and chemical approaches were undertaken. Cross-linkage by irradiation was carried out using a Co⁶⁰ source and a Van de Graaff accelerator.

Synthesis of Organic Binders by Chemical Methods

Synthesis of organic binders for graphite application consisted of investigating dicyclopentadiene as a precursor to a complex resin possessing a high degree of cross-linking.

*C. D. Hurd, *Pyrolysis of Carbon Compounds*, Chemical Catalogue, Inc., New York, 1929.

†J. B. Madison and R. M. Roberts, "Pyrolysis of Aromatics and Related Heterocyclics," *Ind. Eng. Chem.*, Vol. 50, 1958, p. 237.

‡S. L. Madorsky and S. Straus, "Thermal Degradation of Polymers at Temperatures up to 850°C," WADC Technical Report 59-64, June 1959, pp. 1-23.

§B. T. Brooks, et al., *The Chemistry of Petroleum Hydrocarbons*, Vol. 2, Reinhold Publishing Corporation, New York, 1955.

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Dicyclopentadiene is an unsaturated organic liquid that has a boiling point of 170°C, a molecular weight of 132.2, and contains 90.8 percent available carbon in its structure. The unsaturated characteristic of dicyclopentadiene offers a convenient route for polymerization. The catalyzing agents studied for developing cross-linking in dicyclopentadiene were aluminum trichloride, phosphorus pentoxide, sulfur, and trichloroacetic acid. In another study, equal volumes of furfuryl alcohol resin and dicyclopentadiene were mixed and boiled until a syrupy appearing resin was formed.

Sulfur proved to be the most effective of the chemical additives for developing a resinous material. A sulfur-treated dicyclopentadiene gave the highest carbon residue on pyrolysis at 850°C in argon. A comparison of the carbon recoveries obtained from various catalyzed dicyclopentadiene resins is shown in Table 2.3-5.

TABLE 2.3-5
CARBON RESIDUES RESULTING FROM VARIOUS
DICYCLOPENTADIENE RESINS AFTER
PYROLYSIS AT 850°C IN ARGON

Catalyzing Agent	Carbon Residue, %
Aluminum trichloride	7.3
Phosphorous pentoxide	18.0
Trichloroacetic acid	21.2
Sulfur (solid)	25.3
Sulfur (flowers)	46.5
Furfuryl alcohol and dicyclopentadiene	34.0

The dicyclopentadiene resins formed by refluxing with sulfur were used in the fabrication of unfueled graphite bodies to determine their usefulness as graphite binders. As can be seen in Table 2.3-6, the dicyclopentadiene resin used in extrusion No. 249-3 gave a final graphitized density that is comparable to the densities obtained from furfuryl alcohol resins. Also included in the table are the final graphitized densities obtained using various furfuryl resins that were either synthesized in the laboratory or purchased. The final graphitized densities obtained for both the catalyzed and uncatalyzed resins are shown as percent of theoretical density of graphite (2.26 g/cm³).

Synthesis of Organic Binders By Irradiation

Exposure of dicyclopentadiene to gamma radiation to develop cross-linkage through free radical formation was carried out using a Co⁶⁰ source. The exposure rate resulting from the Co⁶⁰ was approximately 8×10^5 r/hr. Samples were irradiated both at room temperature and at 100°C for periods up to 289 hours. The room temperature and 100°C irradiations affected the dicyclopentadiene in the same manner. The clear liquid changed to a yellow color, and approximately an 8-percent increase in volume occurred. Approximately 11 percent of the liquid was changed to a milky semisolid product dispersed throughout the liquid, but without any noticeable change in viscosity. Pyrolysis of the irradiated material at 850°C under argon showed an increase in carbon residue, evidencing cross-linkage through gamma irradiation.

Samples of dicyclopentadiene and furfuryl alcohol were exposed to electron radiation in the Van de Graaff accelerator for 1 hour. The furfuryl alcohol was polymerized in an oxygen-free atmosphere to a viscosity of 2060 centipoise at room temperature and exhibited a carbon recovery of 31 percent following pyrolysis at 850°C in argon. The dicyclopentadiene appeared to be less affected by the 1-hour irradiation in that no noticeable change was observed in viscosity, but on pyrolysis at 850°C under argon an 18.5-percent carbon

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TABLE 2.3-6

GRAPHITIZED DENSITIES OF EXTRUSIONS PREPARED FROM SYNTHETIC BINDERS

Extrusion Number	Binder			Graphitized Extrusion			
	Preparation	Viscosity At 23°C, centipoises	Treatment	Number	Fuel	Fuel Loading, mg U/cm ²	Percent Of Theoretical Density
249-2	Dicyclopentadiene plus 35 wt % sulfur refluxed	600	Uncatalyzed	268	None	None	75.1
249-1	Dicyclopentadiene refluxed through sulfur	960,000	Uncatalyzed	276	None	None	69.7
249-3	Dicyclopentadiene plus 35 wt % sulfur refluxed	1,600	Uncatalyzed	278	None	None	79.8
248	Furfuryl alcohol refluxed through ZrO ₂	19,200	Uncatalyzed	274	None	None	80.1
248	Furfuryl alcohol refluxed through ZrO ₂	19,200	Catalyzed 0.3% TSA ^a	275	None	None	83.2
248	Furfuryl alcohol refluxed through ZrO ₂	19,200	Catalyzed 0.3% TSA	273	(Zr, U) ^c	100	78.4
244	Furfuryl alcohol refluxed through Al ₂ O ₃	1,120	Uncatalyzed	261	None	None	80.0
244	Furfuryl alcohol refluxed through Al ₂ O ₃	1,120	Catalyzed 0.3% TSA	263	None	None	83.8
244	Furfuryl alcohol refluxed through Al ₂ O ₃	1,120	Catalyzed 0.3% TSA	267	(Nb, U) ^c	100	84.4
Karbo ^d 110	-	-	Uncatalyzed	281	None	None	74.2
Karbo 110	-	-	Catalyzed 0.3% TSA	280	None	None	83.0
Karbo 110	-	-	Catalyzed 0.3% TSA	282	(Zr, U) ^c	100	76.8
Karbo 1600	-	-	Uncatalyzed	284	None	None	79.7
Karbo 1600	-	-	Catalyzed 0.3% TSA	283	None	None	83.5
Karbo 1600	-	-	Catalyzed 0.3% TSA	285	(Zr, U) ^c	100	80.0

^aTSA - p-toluenesulfonic acid.^b(Zr, U)C fuel blend 20.2-45-RW, 10 mole % UC, -200/+400 mesh, Tyler series.^c(Nb, U)C fuel blend 19.9-46-RW, 10 mole % UC, -200/+400 mesh, Tyler series.^dKarbo resins from Karbo, Inc., 135 South LaSalle Street, Chicago, Illinois.

recovery was realized. Without the radiation exposure, neither of these pure materials would have given a measurable carbon recovery. Following the 1-hour exposure, dicyclopentadiene was given a 5.5-hour exposure receiving a total dosage of 8.5×10^8 rads. The resulting material was black and syrupy in appearance, and the viscosity rose to 1240 centipoise at room temperature. After pyrolysis at 850°C, the recoverable carbon increased to 23.3 percent of the original weight. Cross-linking by irradiation proved to be a feasible approach and further investigations with other organic compounds are planned.

Synthesis of Compounds of Known Nomenclature

Polybenzylene - Polybenzylene can be derived from benzyl compounds (halide, alcohol, etc.) through the Friedel-Craft reaction with appropriate catalysts. Such products are usually highly branched and generally give rise to an appreciable gel fraction. In an effort to prepare linear polybenzylenes, three reaction schemes were tried. The first used the reactants terephthaloyl and diphenylmethane. The second method used isophthaloyl chloride and diphenylmethane. The third preparation scheme used chloral and diphenylmethane. Each scheme gave rise to a precursor which had to be further reacted to obtain polybenzylene. With the first two reactants, reduction of the ketone groups to methylene was required; while with the precursor prepared from chloral, hydrolysis followed by decarboxylation was required.

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Some of the polybenzylene precursors prepared were found to have sufficiently low melting points to be of interest as extrusion resins. Furthermore, on pyrolysis, some organic compounds gave carbon yields of over 50 weight percent. However, the polybenzylene precursors were not convertible to pure polybenzylene nor did they appear to readily cross-link; consequently, further evaluation was not pursued. The significant parameters used in the preparation of various polybenzylene precursors are shown in Table 2.3-7.

Polycyclohexylenephenylene - Benzene and cyclohexanol react in the presence of BF_3 to provide cyclohexylbenzene (56%) and p-dicyclohexylbenzene (27%). This reaction was the basis for preparing polycyclohexylenephenylene through the use of benzene with 1, 3 - and 1, 4 - cyclohexanediol. It was expected that organic molecules prepared by this method would be largely substituted in the para-position of the benzene ring with some control of the melting point resulting from the use of 1, 3 - or 1, 4 - cyclohexanediol.

Numerous attempts were made to prepare polycyclohexylenephenylene. With one exception, all of the products were low-melting tar or oil. Moreover, none of these products gave a significant carbon residue upon pyrolysis. The one exception was a product that flowed at 195°C and gave a 34-percent carbon residue on thermogravimetric analysis. It was concluded from the results, shown in Table 2.3-8, that polycyclohexylenephenylene does not warrant further consideration for binder resin applications.

Polycyclohexadienylenephenylene - The organic material polycyclohexylenephenylene may be regarded as a partially hydrogenated polyphenyl in which each alternate ring is fully hydrogenated. Polycyclohexadienylenephenylene can be envisioned similarly except that only partial hydrogenation of each alternate ring is indicated. This material was synthesized by reaction of a di-Grignard reagent derived from dihalobenzene both with a 1, 3 - and 1, 4 - cyclohexanedione. The di-Grignard reagent was difficult to prepare. This problem was solved by the use of a step-wise synthesis scheme in which mono-Grignard was formed and reacted, followed by reaction with a second halide. Another difficulty was that cyclohexadienes proved to be thermodynamically unstable with respect to benzene and to cyclohexene.

Synthesis reactions, shown in Table 2.3-9, were carried out in an attempt to build a high molecular weight structure from this metastable material. In these syntheses, the product could not be dehydrated nor further reacted. Therefore, further work on polycyclohexadienylenephenylene synthesis was discontinued.

Homologs of Polyphenylene and Polybenzylene - Some homologs of polyphenylene were investigated to determine the effects of variation in methylene and methyl content on carbonization and cross-linkability, shown in Table 2.3-10. Synthesis schemes were as follows:

1. Polymer XXII was prepared by the decomposition of the mixed, (mono-) Grignards of m-dibromobenzene, α , α' -dibromo-m-xylene and bromobenzene by treatment with cobaltous chloride.
2. Polymer XXI was prepared by Friedel-Craft reaction of α , α' -dibromo-m-xylene and xylene with ferric chloride used as a catalyst.
3. Polymer XXV was prepared by Kovacic's polyphenylene synthesis starting with toluene and utilizing aluminum chloride, cupric chloride, and water as co-catalysts.
4. Polymers XXIV and XXVII were attempted by Friedel-Craft reaction of benzaldehyde with diphenylmethane.

TABLE 2.3-7

A SUMMARY OF REACTANTS USED AND DATA OBTAINED THROUGH THE SYNTHESIS OF POLYBENZYLENE PRECURSORS^a

Synthesis Number	Reactants	Catalyst	Solvent	Melting Point, °C	Molecular Weight	Carbon Residue, % (TGA)	Comments
I	Terephthaloyl chloride-diphenylmethane	AlCl ₃	None	>300	-	-	-
II	Terephthaloyl chloride-diphenylmethane	AlCl ₃	C ₆ H ₅ NO ₂	>300	-	-	-
III	Isophthaloyl chloride-diphenylmethane	AlCl ₃	None	< 96	1200 ^b 430	42 20	Two fractions were obtained which contained acid and acyl halides. The carbonyl group reduced.
VI	Isophthaloyl chloride-diphenylmethane	AlCl ₃	CS ₂	112	1000	52	Attempted reduction yielded a contaminated product. Residue = 40% after attempted cure with dibenzoylperoxide.
X	Isophthaloyl chloride-diphenylmethane	AlCl ₃	CS ₂	74	1160	26	Data are for a partial reduction of the carbonyl group.
IV	Chloral - diphenylmethane	H ₂ SO ₄	H ₂ SO ₄	-	-	-	No reaction.
VIII	Chloral - diphenylmethane	ZnCl ₂	Glacial acetic acid	-	-	-	No reaction.
IX	Chloral - diphenylmethane	H ₂ SO ₄	H ₂ SO ₄	80 ^b 58	997 720	- 58	Precursor Hydrolyzed product

^aGeneral structure^bTwo runs

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TABLE 2. 3-8

A SUMMARY OF REACTANTS USED AND DATA OBTAINED THROUGH THE SYNTHESIS OF POLYCYCLOHEXYLENEPHENYLENE^a

Synthesis Number	Reactants	Catalyst	Solvent	Flow Point	Molecular Weight	Carbon Residue, % (TGA)	Comments
V	1, 4-cyclohexanediol and benzene	BF ₃ ·Et ₂ O	Benzene	Gum	363	0	Residue = 5% after attempted cure with dibenzoylperoxide
VII	1, 4-cyclohexanediol and benzene	ZnCl ₂	Benzene	Oil	-	4	Very low yield
XI	1, 4-cyclohexanediol and benzene	ZnCl ₂	Benzene	-	-	-	No product isolated
XII	1, 4-cyclohexanediol and benzene	ZnCl ₂	Acetic Acid	-	-	-	Obtained ester
XIII	1, 4-cyclohexanediol and benzene	BF ₃ ·Et ₂ O	Benzene	Gum	412	1	
XVI	1, 4-cyclohexanediol and benzene	H ₂ SO ₄	H ₂ SO ₄	Gum	818	2	
XVII	1, 4-cyclohexanediol and benzene	BF ₃	Benzene	-	-	-	No product isolated
XVIII	1, 4-cyclohexanediol and benzene	AlCl ₃	Benzene	195°C	977	34	
XXVII	1, 3-cyclohexanediol and benzene	AlCl ₃	Benzene	-	-	-	No product isolated. Subsequent examination revealed that material used was not 1, 3-cyclohexanediol but an unknown substance mislabeled by the vendor.

^aGeneral Structure

TABLE 2.3-9
A SUMMARY OF REACTANTS USED AND DATA OBTAINED THROUGH THE
SYNTHESIS OF POLYCYCLOHEXADIENYLENEPHENYLENE

Synthesis Number	Compound Sought	Reactants	Solvent	Flow Point, °C	Molecular Weight	Carbon Residue, % (TGA)	Comments
XIV		BrMgC ₆ H ₄ MgBr 1,4-cyclohexanedione	Et ₂ O	-	-	-	Two-stage reaction, second stage did not react.
XXIII		BrMgC ₆ H ₄ Br 1,3-cyclohexanedione	Et ₂ O	145	1370	-	
XV		BrMgCH ₂ C ₆ H ₄ CH ₂ MgBr 1,4-cyclohexanedione	Et ₂ O	-	670	-	Two-stage reaction, second stage did not react.

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TABLE 2.3-10
A SUMMARY OF THE REACTANTS USED AND DATA OBTAINED THROUGH
THE SYNTHESIS OF POLYPHENYLENE AND POLYBENZYLENE HOMOLOGS

Synthesis Number	Compound Sought	Reactants	Solvent	Flow Point, °C	Molecular Weight	Carbon Residue, % (TGA)	Comments
XXII		m-C ₆ H ₄ Br ₂ m-(BrCH ₂) ₂ C ₆ H ₄ BrC ₆ H ₅ Mg CoCl ₂ (cat)	Et ₂ O	130	1500	45	Contains residual Br
XXI		m-(BrCH ₂) ₂ C ₆ H ₄ (CH ₃) ₂ C ₆ H ₄ FeCl ₃ (cat)	Nitro-benzene	150	2800	27	Contains 2.95% residual Br
XXV		Toluene AlCl ₃ H ₂ O CuCl ₂	None	300	-	-	
XXIV		Benzaldehyde Diphenylmethane	H ₂ SO ₄	-	-	-	No product isolated
XXVII		Benzaldehyde Diphenylmethane + AlCl ₃	Nitro-benzene	-	-	-	Crosslinked insoluble gel

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None of the soluble organic compounds were cross-linked by reactions with dibenzoyl peroxide or di-t-butyl peroxide. The material shown in synthesis No. XXII had the highest carbon yield, indicating that the lower concentrations of aliphatic groupings were more desirable.

In summary, a number of low-melting, aromatic, organic compounds having relatively high molecular weights was synthesized. However, attempts to cross-link these organic compounds by peroxide cures were not completely successful. The failure to develop a sufficient degree of cross-linking may have been the major reason for the relatively low-carbon yields. However, in synthesis Nos. III, VI, IX, and XXII the organic compounds produced gave carbon yields in ranges that may prove worthy of further investigation in an effort to find pure compounds having well-defined physical properties.

SUMMARY AND CONCLUSIONS

Studies on (Zr, U)C containing 52, 28.5, and 20.2 weight percent uranium showed that as the uranium content is decreased, there is a concurrent increase in fuel stability. Using complex (Zr, U)C fuels containing 20.2 weight percent uranium, it is possible to graphitize fuel bodies to temperatures as high as 2400°C without affecting the stability of the fuel.

Stability studies as a function of graphitizing temperature on (Nb, U)C fuels exhibited a similar trend to that observed for the (Zr, U)C fuels. It appears that graphitized fuel elements (Nb, U)C containing approximately 20 weight percent uranium can be graphitized to temperatures as high as 2600°C with no major loss of stability. It was also observed that particles of (Nb, U)C show greater resistance to attack by furfuryl alcohol resin products during the carbonization cycle.

Solid-state carburization of Zr-U alloy in graphite matrices showed that complete in-situ carbonization to a single-phase (Zr, U)C occurred after 1 hour at 2200°C. Carburization for 1 hour at 2600°C continued to yield a solid solution of (Zr, U)C, but with a trace of UC₂ detected by X-ray diffraction analysis. Increasing the fuel carburization temperature to 2800°C produced a fuel containing two solid solution (Zr, U)C phases and a general reduction of fuel particle size, but no evidence of UC₂ formation. Chemical analysis showed no significant loss in uranium content from the graphite fuel element when graphitized to temperatures as high as 2800°C.

Good quality Zr-U alloy spheres were prepared using an inductively coupled argon plasma. Chemical analysis showed only minor losses of uranium from the alloy during spheroidization.

Several binder compositions were prepared. The use of some of these binders in preparing graphite extrusions resulted in appreciable density increases.

PLANS AND RECOMMENDATIONS

Efforts to produce a single-phase, high-density, in-situ carburized (Zr, U)C fuel will continue, and its compatibility with graphite matrices at various temperatures will be studied using electron microprobe and X-ray diffraction analyses. Spheroidization of various Zr-U alloys will be continued using an inductively coupled argon plasma as a heat source. Throughout all spheroidization studies, special precautions will be taken to minimize oxygen and nitrogen contamination. The potential of in-situ carburized Zr-U alloy as a fuel-bearing constituent for high-temperature graphite application will be explored in an effort to develop a stable high-temperature fuel.

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Evaluation of graphite binders synthesized in the laboratory both by chemical and irradiation techniques will be continued. Continued efforts will be made to improve the density and internal structure of fueled and unfueled graphite bodies. These efforts will include a study on various available graphites as well as the synthesis of various carbons and graphites by laboratory means. Attention will be given to mixing, extrusion variables, and graphitizing conditions.

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3. STABILIZED CERAMIC FUEL ELEMENTS

In this section the progress is reported on four programs, three of which were terminated at the end of Fiscal Year 1963 and one of which was initiated at the start of FY-64. This latter program, Burnup Capabilities of Y_2O_3 -stabilized UO_2 and Stabilized Fuel - BeO Matrix Materials (57068), is directed toward assessing the high-burnup capabilities of such systems and to complete those studies, initiated in the FY-63 programs, which require additional investigation. To simplify the reporting on these programs for the Calendar Year 1963, each task is reported as an entity with one exception, the plans and recommendations for all phases are included under Job 57068 as it is the continuing program.

3.1 BURNUP CAPABILITIES OF Y_2O_3 -STABILIZED UO_2 AND STABILIZED FUEL — BeO MATRIX MATERIAL (57068)

The objective of this program is to determine the effect of high fuel burnup on stabilized UO_2 fuel systems as such and as sources of fuel in BeO-base fuel elements. In addition, the necessary laboratory bench tests will be performed in support of the in-pile test program.

Previous in-pile testing of BF-116 compositions resulted in a moderate fuel burnup (6×10^{19} fissions/cm³).^{*} High-burnup (2 to 4×10^{20} fissions/cm³) tests are needed to determine the physical integrity and fission-product-release characteristics of these fuel elements. The compositions selected for these tests include specific UO_2 loadings chosen to produce both semicontinuous and discontinuous fuel phases in a BeO matrix. The test results should indicate if continuity of the fuel phase influences physical integrity and fission-product release. The test specimens for this study have been extruded and most of the coating work is complete.

FABRICATION OF TEST SPECIMENS

The fuel compositions for the test specimens were reacted for 1 hour at 1850°C in air and ball-milled for 100 hours to an average particle size of 4 to 5 microns; the maximum size is about 30 microns. The milled fuel compositions were incorporated into UOX-grade BeO, extruded into tubular shape, and sintered at 1675°C for 2 hours in hydrogen (dew-point, 0°C) to densities above 99 percent of theoretical. The densified specimens were then clad with Y_2O_3 -stabilized ZrO_2 using vapor-deposition techniques developed under Job 57062 (see section 3.2). The as-deposited coatings contained more than 25 weight percent Y_2O_3 , in essentially the stable cubic form, with a trace of monoclinic phase. The compositions being studied, along with their status, are given below; all compositions contain enriched (93.2% U^{235}) UO_2 .

^{*}G. T. Muehlenkamp, "Ceramic Reactor Materials," GE-NMPO, APEX-914, June 15, 1962, p. 141.

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BF-204 Specimens

Two compositions using the F-204 ($45\text{UO}_2 - 35.6\text{Y}_2\text{O}_3 - 19.4\text{ZrO}_2$)* fuel additive to give UO_2 loadings of 20.5 and 9.67 weight percent in BeO are to be tested. These specimens are designated 20BF-204 and 9.5BF-204, respectively. All were coated with vapor-deposited Y_2O_3 -stabilized ZrO_2 , and are awaiting irradiation in the ETR.

BF-216 Specimens

The fuel additive F-216 ($65\text{UO}_2 - 22.6\text{Y}_2\text{O}_3 - 12.4\text{ZrO}_2$) was incorporated in BeO to give UO_2 loadings of 20.22 and 15.1 weight percent. These compositions are designated 20BF-216 and 15BF-216, respectively. The Y_2O_3 -stabilized ZrO_2 coating was vapor-deposited on all samples, which are awaiting irradiation in the ETR.

$\text{UO}_{2+x} \cdot 3\text{Y}_2\text{O}_3$ Cladding on BeO

Enriched $\text{UO}_{2+x} \cdot 3\text{Y}_2\text{O}_3$, 0.0076-centimeter thick, was coextruded on the bore of a BeO tube. The tube was cut into specimens about 15 centimeters long and the bore of each was then dip-coated with 0.0051 centimeter of BeO. These specimens are awaiting dynamic testing at the LITR. Similar specimens are being prepared for high-burnup testing in the ETR.

IRRADIATION TESTING

Irradiation testing of F-204 in a BeO matrix has been underway since the second quarter of FY-63. A static irradiation test of 20BF-204-Gd, designated 33MT-84, in the ETR was completed (Table 3.1-1). LTC-68, a dynamic test run in the LITR, in support of ETR test 33MT-84, was also completed and is reported in detail later in this section of the report. Table 3.1-1 presents results of the 33MT-84 test and indicates the status of other planned high-burnup tests. The testing program is designed to provide the necessary evaluation of a range of fueled BeO compositions which produce semi-continuous and discontinuous fuel phases. The effect of high burnup on both physical integrity and fission product retention will be studied as a function of continuity of the fuel phase.

In addition to the high-burnup tests, one dynamic test (LTC-72) will be run in the LITR in support of 33MT-124 and 33MT-126. The objective of the LTC-72 dynamic test is to determine the rate at which fission products escape from the BeO and the effects of irradiation on physical integrity; testing will be done at 1250°C for a minimum of 2 weeks.

Static Irradiation Test, 33MT-84

A detailed description of test number 33MT-84, a static irradiation test in the ETR, was presented in a monthly progress report.† Three tubular specimens, designated 20BF-204-Gd, contained 20.5 weight percent UO_2 (93.2% U^{235}) and 1 weight percent Gd_2O_3 in a BeO matrix. This is fuel composition F-204 modified by addition of the Gd_2O_3 ($45\text{UO}_2 - 33.35\text{Y}_2\text{O}_3 - 2.25\text{Gd}_2\text{O}_3 - 19.4\text{ZrO}_2$). The Gd_2O_3 , substituted directly for the Y_2O_3 , amounted to 1 percent.

The test assembly was irradiated for 1688 hours in the temperature range 1175° to 1370°C . Fuel burnup calculated from Cs^{137} data was 3.15×10^{20} fissions/ cm^3 of total fuel element, the highest burnup yet sustained by this kind of ceramic fuel element. The elements maintained approximately 70 percent of their as-fabricated strength (2650 kg/cm^2), and there were essentially no changes in dimensions or density.

* Unless otherwise noted, all compositions are in weight percent.

† "High-Temperature Materials Program Progress Report No. 22, Part B," GE-NMPO, GEMP-22B, April 30, 1963, pp. 32-34.

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TABLE 3.1-1

ETR IRRADIATION TEST PROGRAM FOR HIGH BURNUP AT 1250°C

Test Number	Specimen Composition				Status	Irradiation Data		Burnup, fissions/cm ³	
	Designation ^b	Weight Percent ^c		BeO		Time On Test	Temperature, °C	Desired	Calculated
		UO ₂	Fuel Additive						
33MT-84 ^a	20BF-204Gd	20.18	45.9	54.1	Test complete	1688 hrs	1175-1370	2 to 5 x 10 ²⁰	3.15 x 10 ²⁰
33MT-109	20BF-204	20.5	47.7	52.3	Capsule fabricated	-	-	2 x 10 ²⁰	-
33MT-114	20BF-204	20.5	47.7	52.3	Capsule fabricated	-	-	4 x 10 ²⁰	-
33MT-120	9.5BF-204	9.67	22.5	77.5	Capsule fabricated	-	-	2 x 10 ²⁰	-
33MT-121	9.5BF-204	9.67	22.5	77.5	Capsule fabricated	-	-	4 x 10 ²⁰	-
33MT-117	20BF-216	20.22	31.9	68.1	Capsule fabricated	-	-	2 x 10 ²⁰	-
33MT-118	20BF-216	20.22	31.9	68.1	Capsule fabricated	-	-	4 x 10 ²⁰	-
33MT-124	X-phase on BeO	Inhomogeneous fuel element ^d			In fabrication	-	-	4 x 10 ²⁰	-
33MT-126	X-phase on BeO	Inhomogeneous fuel element ^d			In fabrication	-	-	2 x 10 ²⁰	-
33MT-123	15BF-216	15.10	23.8	76.2	In fabrication	-	-	4 x 10 ²⁰	-
33MT-125	15BF-216	15.10	23.8	76.2	In fabrication	-	-	2 x 10 ²⁰	-

^aCartridge design shown as Figure 5.6, "High-Temperature Materials Program Progress Report No. 22, Part B," GE-NMPO, GEMP-22B, April 30, 1963, p. 34.

^bAll BF compositions were extruded followed by vapor coating with 0.0025 cm of yttria-stabilized zirconia with the exception of 33MT-84, -124, and -126; 33MT-84 is uncoated; and 33MT-124 and -126 will be dip-coated on the ID only with 0.005 cm of BeO.

^cFuel additive composition, in weight percent. UO₂ percentages in BF compositions are from chemical analysis. Fuel additive and BeO percentages were calculated from UO₂ analyses. The fuel particle size used in this test program averaged about 4 to 5 microns with the maximum size being about 30 microns.

	Composition, wt %			
	UO ₂	ZrO ₂	Gd ₂ O ₃	Y ₂ O ₃
F-204Gd	45	19.4	2.25	33.35
F-204	45	19.4	-	35.6
F-216	65	12.4	-	22.6

^dUO_{2+x}·3Y₂O₃ was coextruded as 0.0076 cm clad on the ID of a BeO tube and subsequently dip-coated with 0.005 cm BeO.

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Post-Irradiation Analysis - The capsule was inadvertently opened at Idaho resulting in loss of the fission gases prior to shipment to Evendale. Figure 3.1-1 shows the tubes before and after irradiation. There was one small chipped area on the end of one tube but the other two tubes were intact; the surface appearance of all tubes was good. The weight, density, and dimensional changes after irradiation are summarized in Table 3.1-2. The weight losses varied from about 0.5 to 1.5 percent which amounts to 2.7 to 7.5 percent loss as UO_2 , assuming all weight loss is due to UO_2 loss. Laboratory testing predicted a UO_2 loss from these fuel elements of about 1.5 percent. Chemical analyses will be made to determine the validity of the weight loss measurements. The dimensional changes are negligible for a test of this duration. Strength measurements before and after test are shown in Table 3.1-3. The measurements show that the fuel elements retained about 70 percent of the as-sintered strength. A bench test now in progress will determine whether this decrease is due to the thermal treatment or to the irradiation. The lack of agreement in values obtained at the two different spans (Table 3.1-3) can best be explained by the tendency of the as-sintered specimens to crush due to the short span and the thin wall of the tubes resulting in more of a crushing strength measurement than a modulus-of-rupture measurement. The irradiated tubes measured on the 4.45-centimeter span did not crush, but they did break at large angles to the direction of load, again indicating a questionable modulus-of-rupture measurement.

TABLE 3.1-2
PRE- AND POST-IRRADIATION WEIGHT, DENSITY, AND
DIMENSIONAL DATA^a FOR ETR TEST 33MT-84

Specimen Designation	Weight, g		Fuel Loss, ^b %	Density			Length			Outside Diameter		
	Before Test	After Test		Before Test, g/cm ³	After Test, g/cm ³	Decrease, %	Before Test, cm	After Test, cm	Decrease, %	Before Test, cm	After Test, cm	Increase, %
441-E-38	5.3160	5.2664	4.62	4.056	4.004	1.3	8.888	8.951	0.7	0.6982	0.6995	0.2
441-E-40	5.4527	5.3699	7.52	4.082	3.998	1.6	8.894	8.966	0.8	0.6982	0.7013	0.4
441-E-54	5.4208	5.3910	2.72	4.056	3.995	1.5	8.880	8.936	0.6	0.6993	0.7013	0.3

^aThere was no change in inside diameter measurements within the accuracy of the measurements (± 0.0025 cm).

^bAssuming all loss as UO_2 .

Dynamic Test LTC-68

A detailed description and drawing of **LITR test LTC-68** of two 20BF-204-Gd tubes with hexagonal external configuration was reported previously.* The composition tested was the same as described above for the 33MT-84 assembly. The specimens were on test for a total of 1193 hours in the temperature range from 1150° to 1370°C. The test was originally scheduled to run for 2 weeks at 1370°C; however, until some of the gadolinia burned up at about 785 hours, the test operated below the desired temperature. Sequentially, this test operated approximately 150 hours at 1150° to 1225°C, 470 hours at 1225° to 1300°C, 165 hours at 1300° to 1350°C, 240 hours at 1350° to 1370°C, and 168 hours at 1150°C. The fission product release, while the temperature was in the range from 1350° to 1370°C, initially increased and then was constant for the remainder of the 240 hours while the temperature was 1370°C. This increase in release was probably caused by diffusion of the fission gases and iodine from the BeO fuel element. When the temperature was reduced to 1150°C during the last 168 hours, the level of fission product release decreased to that amount due only to recoil. Fission product release from this test is discussed further in section 3.4 of this report.

The modulus-of-rupture strength of the irradiated specimens was 2240 kg/cm² (upstream specimen) and 2540 kg/cm² (downstream specimen). These values compare very

*"Second Annual Report—High-Temperature Materials and Reactor Component Development Programs, Volume II—Materials," GE-NMPO, GEMP-177B, February 28, 1963, pp. 88-89.

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GE-NMPO

Neg. P63-3-4

BEFORE IRRADIATION

Neg. RML 2175

AFTER IRRADIATION

Fig. 3.1-1 — Photographs of 33MT-84 specimens before and after irradiation to a burnup of 3.15×10^{20} fissions/cm³

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TABLE 3.1-3
MODULUS OF RUPTURE OF 20BF-204-Gd TUBES,
STATIC IRRADIATION TEST 33MT-84

Tube Treatment	No. Of Measurements	Modulus Of Rupture, kg/cm ²		
		Maximum	Minimum	Average
As-sintered (7.62-cm span)	3	2735	2600	2650
As-sintered (4.45-cm span)	2	1655	1375	1515
After irradiation (7.62-cm span)	1 ^a	-	-	2095
After irradiation (4.45-cm span)	3	1100	950	1035

^aAnother value (1450 kg/cm²) was obtained but is not presented here; tube used to obtain this value was cracked and chipped on one end, and it crushed during the modulus-of-rupture measurement, instead of breaking between the supports.

favorably with the average modulus of rupture of 2180 kg/cm² for unirradiated specimens. The strengths obtained before and after irradiation are typical of fine-grained microstructures and indicate little or no change resulting from the test. Since weight change measurements indicated less than 1 percent loss of UO₂, no chemical analysis was made. No significant change in dimensions or density resulting from irradiation occurred.

SUMMARY AND CONCLUSIONS

The irradiation of BeO fueled to 20 weight percent UO₂ with the Gd-modified F-204 composition has shown that these fuel elements retained about 70 percent of their strength after irradiation to 3.15×10^{20} fissions per cm³ of fuel element and that dimensional changes were negligible. Six additional cartridges for long-term irradiation tests have been assembled and shipped to the ETR.

PLANS AND RECOMMENDATIONS

The ETR high-burnup static irradiations program will start with the January ETR cycle. Six of the ten irradiations are scheduled for insertion in this cycle. Evaluation of the 33MT-84 static irradiation capsule of the 20BF-204-Gd, gadolinia-modified fuel composition, will be completed early this year. A dynamic test of the coextruded UO_{2+x}·3Y₂O₃ composition on BeO will be run in the LITR early this calendar year to evaluate fission product release rate and physical integrity of the fuel elements. The bench testing program for all of these tests will be started and will include measurement of physical properties before and after heat treatment for extended periods of time. After the vapor coating work is completed for test specimens for this Job and for Job 57064, (Coated Fuel Particle Development and Evaluation), the program for reducing the Y₂O₃ content of these coatings while maintaining the cubic ZrO₂ structure will be re-activated. Diffusion studies of I¹³¹ and Xe¹³³ will be continued on selected UO₂-Y₂O₃ and UO₂-Y₂O₃-ZrO₂ compositions as such and as a source of fuel in BeO. Work will be started to identify the liquidus temperature in the BeO-F-204 system.

3.2 COATINGS FOR CERAMIC FUEL ELEMENTS (57062)

The objective of this program was to delineate coating process parameters for reproducibly applying vapor-deposited ceramic coatings to fueled ceramic composites and to evaluate the capability of the resulting coatings for inhibiting fission product release during in-pile testing for extended periods of time at very high temperatures.

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Cubic-phase (Y_2O_3 -stabilized) ZrO_2 coatings were applied to fueled BeO tubular elements by co-deposition of Y_2O_3 and ZrO_2 from the reaction of the vapors of YCl_3 and ZrCl_4 with H_2O vapor provided by the reaction of H_2 and CO_2 .

Studies made during CY-62 resulted in establishment of methods for specimen surface-preparation, design of the coating apparatus, and delineation of coating process parameters for reproducibly applying dense, adherent Y_2O_3 -stabilized ZrO_2 coatings by vapor deposition.

During CY-63, additional experiments with the Y_2O_3 -stabilized ZrO_2 coating process were made, and methods to lower the Y_2O_3 content were investigated. Fueled BeO tubes coated with cubic ZrO_2 were evaluated in in-pile and bench tests to determine physical and chemical integrity. The feasibility of coating tubes with vapor-deposited BeO was established.

COATING PROCESS INVESTIGATIONS

The Y_2O_3 - ZrO_2 deposition rate in coating internal surfaces of tubes is known to be controlled by the rate of H_2O vapor formation.* Using the parameters in Table 3.2-1, experiments were performed in which the external surfaces of fueled BeO tubes were coated with vapor-deposited cubic ZrO_2 at varied specimen temperatures between 1200° and 1250°C. Figure 3.2-1, an Arrhenius plot of the data, indicates that the temperature-dependence of the H_2O formation rate is approximately the same as the temperature-dependence of the deposition rates during coating of either the external or the internal surface. The water-formation rate curves (in arbitrary units) are drawn through the experimental points with a slope calculated from the activation energy for water formation from H_2 and CO_2 , given as 57 kcal/mole by Graven and Long.† The greater deposition rate for external coatings is partially due to the higher ZrCl_4 and YCl_3 vapor flow rates used in the external coating experiments, and to the greater residence time of the reaction gases in the specimen heater assembly used for external coatings.

Concentration of Y_2O_3 in Y_2O_3 - ZrO_2 Coatings

Cubic (Y_2O_3 -stabilized) ZrO_2 coatings were examined with an electron microprobe to determine the concentration of Y_2O_3 . The concentration ranged from 24 to approximately 40 weight percent; the latter being the amount expected from the relative chloride flow

TABLE 3.2-1

PROCESS PARAMETERS FOR VAPOR-COATING FUELED BeO
TUBES WITH CUBIC (Y_2O_3 -STABILIZED) ZrO_2

Test Conditions	Process Parameters		
	Internal	Common	External
Run time, min	-	60	-
System pressure, mm of Hg	35-40	-	11-15
H_2 flow, standard ml/min	-	335	-
CO_2 flow, standard ml/min	-	565	-
Ar flow, standard ml/min	-	180	-
(flow for each chloride)			
HCl flow, standard ml/min	20	-	40
Zr metal temperature, °C	-	650	-
YCl_3 temperature, °C	-	890	-

*"Second Annual Report - High-Temperature Materials and Reactor Component Development Programs, Volume II - Materials," GE-NMPO, GEMP-177B, February 28, 1963, p. 159.

†W. M. Graven and F. J. Long, "Kinetics and Mechanisms of the Two Opposing Reactions of the Equilibrium $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$," *Journal of American Chemical Society*, Vol. 76, 1954, p. 2602.

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Fig. 3.2-1 – Deposition rate of cubic ZrO_2 on fueled BeO tubes as a function of the reciprocal of the absolute temperature.

rates used in the coating runs. Each of these coatings was identified by X-ray diffraction analysis as cubic ZrO_2 . It is well known that at least 12 to 15 weight percent Y_2O_3 is necessary to stabilize ZrO_2 in the cubic form* and that cubic ZrO_2 can be found (from phase equilibria relationships) up to approximately 55 weight percent Y_2O_3 . Earlier work indicated that YCl_3 condensation, prior to reaching the specimen to be coated, precluded formation of sufficient Y_2O_3 to stabilize the ZrO_2 coatings. Adjusting the YCl_3 flow rate and eliminating the condensation led to the range of Y_2O_3 concentrations found in this study.

Previous studies of coated tubes heated in air at 1510°C showed that the alpha count increases markedly at this temperature, indicating a diffusion of fuel into the coating.† Since the high Y_2O_3 content of the coating may have enhanced the diffusion, an investigation was begun of means of lowering the Y_2O_3 content of the coatings while maintaining the cubic structure. The results of this study (summarized in Table 3.2-2) indicate that the coatings on specimens downstream of the reaction gas stream contained more Y_2O_3 than those upstream, suggesting that ZrO_2 tends to deposit upstream, while Y_2O_3 tends to deposit downstream. This would account for the presence of free Y_2O_3 in the high- Y_2O_3 experiments (YCSI and YCSII) and cubic ZrO_2 in the low- Y_2O_3 experiments.

Heating the coated tubes in flowing dry air at 1500°C for 72 hours increased the amount of cubic-phase ZrO_2 found in the coatings; e. g., the coating on the downstream tube from run No. YCSIV (Table 3.2-2) was converted from monoclinic to major cubic with a trace of monoclinic phase at the center of the tube.

BeO Vapor Deposition

Three coating experiments were performed in which BeO was vapor-deposited on BeO tubes using equipment and techniques similar to those used in coating with ZrO_2 . To demonstrate in as simple a manner as possible the feasibility of vapor-depositing BeO on a fueled BeO substrate, the experiments were conducted at atmospheric pressure, thereby eliminating the need for a vacuum system. The BeO was deposited from BeCl_2 produced by the reaction of anhydrous HCl gas and Be metal. Although BeO was deposited on the internal surfaces of the BeO tubes in each of the three experiments, the coatings

* E. S. Funston, "Basic Materials Studies: Sinterable High-Purity ZrO_2 Final Report," GE-NMPO, APEX-685, August 1961, p. 6.

† "High-Temperature Materials Program Progress Report No. 26, Part B," GE-NMPO, GEMP-26B, August 16, 1963, p. 12.

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TABLE 3.2-2
RESULT OF THE VARIATION OF Y_2O_3 CONTENT ON COATING STRUCTURE

Run Number	YCl_3 Temperature, °C	Tube Position	Y_2O_3 , wt %		Phases Present At Center Of Tubes By X-Ray Diffraction		
			Calculated	Analyzed ^a	As-Coated	Heated At 1370°C For 48 Hours	Heated At 1500°C For 72 Hours
YCSI	890	Upstream		35.0	Major cubic ZrO_2 , trace Y_2O_3		
		Downstream	77 ^b	100.0	Cubic (Y_2O_3 -rich)	Not determined because of low $ZrCl_4$ evolution ^b	
YCSII	890	Upstream		5.5	Monoclinic ZrO_2	Major monoclinic, trace cubic	Equal amounts monoclinic and cubic
		Downstream	36	27.0	Cubic (Y_2O_3 -rich)		
YCSIII	830	Upstream		5.5	Monoclinic	Major monoclinic, trace cubic	Major monoclinic, minor cubic
		Downstream	22	13.0	Major cubic, trace monoclinic		
YCSIV	810	Upstream		0.10	Monoclinic	Major monoclinic	Major monoclinic, trace cubic
		Downstream	12	8.4	Major monoclinic, trace cubic	Major monoclinic, trace cubic	Major cubic, trace monoclinic

^aWet-chemical analysis.

^b $ZrCl_4$ evolution was one-half that evolved in other runs due to HCl flow rate error.

were thin and lacked uniformity. Equipment was assembled for vapor-coating with BeO using reduced system pressure; however, operation of this apparatus was suspended in favor of coating specimens for the high-burnup program (section 3.1).

PREPARATION OF COATED TUBES FOR EVALUATION

Several groups of BeO tubes (both fueled and unfueled) were coated for use in reactor test LTC-69, thermal testing, and for evaluation by Lawrence Radiation Laboratory at Livermore.

Reactor Test LTC-69

For use in reactor test LTC-69,* which was run to test the effectiveness of the Y_2O_3 - ZrO_2 cladding in minimizing fission product release during reactor operation, 13 tubes of 6BF-204 were coated on the external and internal surfaces with vapor-deposited Y_2O_3 -stabilized ZrO_2 . The fuel phase was incorporated in the BeO matrix in the form of spheres 25 to 53 microns in diameter.

All tubes were etched for 12 minutes in a boiling 1 + 1 mixture of H_2SO_4 - $HClO_4$ prior to coating. The coatings were applied using the equipment and techniques described previously;† the parameters listed in Table 3.2-1 were used. The tube bores were coated at a temperature of 1350°C, and the external surfaces were coated at a temperature of 1235°C. The coating thicknesses and alpha counts for the six tubes selected for LITR test LTC-69 are given in Table 3.2-3. The coatings were dense, crystalline, adherent, and provided complete coverage. Zyglo inspection revealed no cracking; however, ultrasonic inspection showed areas of defective bonding on some external surfaces. The external coatings were generally thicker near the upstream ends of the tubes; the internal coatings were generally uniform in thickness. Figure 3.2-2 shows a transverse section of cubic ZrO_2 on the internal and external surfaces of a tube.

*Results of LTC-69 are reported in section 1.4 of this report.

†"Second Annual Report—High-Temperature Materials and Reactor Component Development Programs, Volume II—Materials," GE-NMPO, GEMP-177B, February 28, 1963, p.148.

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Neg. 3073

INTERNAL SURFACE

250 X

Neg. 3074

EXTERNAL SURFACE

250 X

Fig. 3.2-2—Similar vapor-deposited cubic ZrO_2 coatings on the internal and external surfaces of 6BF-204E tubes

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TABLE 3.2-3
RESULTS OF COATING 6BF-204E TUBES WITH CUBIC (Y_2O_3 -STABILIZED) ZrO_2

Tube	Surface Coated	Coating ^a Thickness, cm	Alpha Counts After Coating, cpm		Alpha Counts After Heating, ^b cpm	
			Upstream End	Downstream End	Upstream End	Downstream End
452E11	Internal	0.0020	4	9	11	6
	External	0.0015	102	723	348	976
452E30	Internal	0.0025	3	7	2	9
	External	0.0020	18	19	261	413
452E36	Internal	0.0025	13	16	7	2
	External	0.0015	62	33	106	126
452E44	Internal	0.0020	18	7	12	1
	External	0.0020	173	162	276	378
452E45	Internal	0.0023	214	38	165	13
	External	0.0028	9	14	163	158
452E54	Internal	0.0020	5	9	34	19
	External	0.0020	34	75	254	294

^aAverage thickness calculated from the coating weight.

^bAlpha counts were taken after heating the coated tubes in air for 1 hour at 1510°C. Uncoated tubes of the same composition showed alpha counts of about 40,000 cpm for the external surface and about 8000 cpm for the internal surface.

Coating Tubes for LRL

Six BeO tubes and six 6BF-204E tubes were vapor-coated with about 0.0025 centimeter of Y_2O_3 -stabilized ZrO_2 and shipped to Lawrence Radiation Laboratory for evaluation. Three tubes of each composition were clad on the internal surfaces only and three of each composition were fully clad.

THERMAL EVALUATION OF COATED TUBES

A group of 6BF-204E tubes * totally coated with about 0.002 centimeter of Y_2O_3 -stabilized ZrO_2 , was aged in flowing dry air for 336 hours. Two coated tubes each were tested at 1250°, 1370°, and 1510°C. Weight change data plotted as a function of time at temperature are shown in Figure 3.2-3 along with data for uncoated tubes tested under the same conditions. At 1250°C the coating retarded the oxidation of the fuel. At 1370°C, there was no significant difference in the oxidation rates between the coated and uncoated specimens. The improved fuel retention resulting from the coating is readily apparent in comparing the weight change curves for coated tubes tested at 1510°C with those for uncoated tubes tested at the same temperature. Modulus-of-rupture, alpha count, and BeO grain size measurements on the aged pieces are listed in Table 3.2-4 along with total weight change. The alpha count rate showed a decrease with time for the coated tubes heated at 1250°C and 1370°C, probably due to volatilization of fuel in or on the coatings. The significant rise in alpha count shown by the coated tubes heated at 1510°C is evidence of fuel migration into the coating.

SUMMARY AND CONCLUSIONS

Studies of the Y_2O_3 -stabilized ZrO_2 coating process show that the coating deposition rate is controlled by the rate of H_2O formation; progress was made in lowering the Y_2O_3 content of these coatings. A topical report on this terminated task is being prepared.

* BeO fueled with F-204 spheres 25 to 53 microns in diameter to give 6 weight percent UO_2 .

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Fig. 3.2-3—Weight change of 6BF-204E tubes as a function of time at temperature in flowing dry air

TABLE 3.2-4

RESULTS OF THERMALLY AGING COATED 6BF-204E^a TUBES FOR 336 HOURS

Aging Temperature, °C	Coating Status	Total Weight Change, %	Alpha Count, cpm ^b				Modulus Of Rupture, ^c kg/cm ²			BeO Grain Size, ^d microns
			Internal Surface		External Surface		Maximum	Minimum	Average	
			Initial	Final	Initial	Final				
1250	Coated	+0.03	12	6	543	519	2100	1220	1575	23
	Uncoated	+0.14	-	-	-	-	1700	1560	1615	35
1370	Coated	+0.10	39	13	776	508	1335	1225	1265	23
	Uncoated	+0.20	-	-	-	-	1470	1400	1435	35
1510	Coated	+0.10	17	34	284	766	1335	1265	1310	39
	Uncoated	-0.05	-	-	-	-	1355	1095	1235	42

^aBeO fueled with 25- to 53-micron F-204E spheres to give 6 weight percent UO₂. The tubes were totally coated with about 0.02 mm vapor-deposited cubic ZrO₂.

^bThe alpha count for uncoated tubes of the same composition is about 40,000 cpm for the external surface and about 8,000 cpm for the internal surface.

^cThe numbers reported are averages of 4 measurements each. The measurements were made using 4-point loading with a 4.45-cm span and a 0.15-cm-per-minute ram travel.

^dBeO grain size in an as-sintered tube of the same composition measured about 25 microns.

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3.3 STABILIZATION OF UO_2 IN CERAMIC FUEL ELEMENTS (57066)

The objectives of this program were to study the chemistry of stabilized UO_2 fuel systems and to develop their capability as a source of fuel in BeO-base fuel elements for extended service in various atmospheres at high temperatures.

Areas of investigation discussed under this heading include measurements of compressive creep, thermal expansion, and vapor pressure. In addition, data on fuel retention of several stabilized UO_2 -BeO compositions and phase relations in the $UO_2 + x \cdot Y_2O_3$ -ZrO₂ system are included.

COMPRESSIVE CREEP STUDIES

During CY-63, more knowledge was gained about the effect of fuel content and BeO grain size on the compressive creep behavior of fueled BeO materials. Fueled BeO with UO_2 contents of 2, 6, 10, 15, and 20 weight percent (added as the F-204 composition) were sintered at 1675°, 1725°, and 1775°C for 2 hours in hydrogen having a dew point of 0°C, to obtain three different BeO grain sizes for each UO_2 content. The sintered densities were all in excess of 98 percent of theoretical. The three grain sizes for each of the five compositions are given in Table 3.3-1.

TABLE 3.3-1
COMPOSITION AND GRAIN SIZE
OF COMPRESSIVE CREEP SPECIMENS

Material	UO_2 Content, wt %	Sintered Grain Size, microns		
		1675°C	1725°C	1775°C
2BF-204	2	28	40	50
6BF-204	6	18	26	43
10BF-204	10	11	14	41
15BF-204	15	8	14	16
20BF-204	20	7	11	22

Creep-rate - stress relationships were determined for each material at 1300°, 1400°, and/or 1500°C. The creep rates were measured at increasing stress levels at each temperature; each stress was maintained for 3 to 4 hours at 1400°C and 1500°C, and for 16 to 72 hours at 1300°C.

Typical results for the creep-rate - stress relationships at 1400°C for the different compositions sintered at 1725°C are shown in Figure 3.3-1. The creep rates of these compositions are plotted in Figure 3.3-2 as a function of the parameter, stress/(grain size)², to illustrate the dependency of creep rate on grain size. The creep rates of compositions sintered at 1675°C and 1775°C show similar relationships.*† The creep rates for each fuel content are approximately linear with stress; also, the rates increase with increasing fuel content, largely due to the decrease in grain size as shown by the linearity of the plot of creep rate versus the parameter, stress/(grain size)². At fuel loadings of 15 to 20 weight percent UO_2 , the increase in creep rate above that due to the grain size effect would appear to be because of the contribution of the more plastic fuel phase at the grain boundaries.

Long-time compressive creep curves were determined for the different fueled BeO compositions to define differences in the fuel phase contribution. The specimens were sintered at 1675°C for 2 hours in hydrogen having a dew point of 0°C to densities above 98 percent of theoretical. The creep measurements were made at a low temperature (1300°C) to

*"High-Temperature Materials Program Progress Report No. 24, Part B," GE-NMPO, GEMP-24B, June 28, 1963, p. 32.

†"High-Temperature Materials Program Progress Report No. 30, Part B," GE-NMPO, GEMP-30B, December 31, 1963, pp. 27-28.

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Fig. 3.3-1—Creep rate at 1400°C of specimens sintered at 1725°C with different fuel content as a function of stress and grain size

Fig. 3.3-2—Creep rate at 1400°C of specimens sintered at 1725°C with different fuel content as a function of stress and grain size

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eliminate the effects of grain growth and fuel loss. The creep curves at 280 kg/cm² for fueled BeO containing 2, 6, 10, and 20 weight percent UO₂ are given in Figure 3.3-3. The creep rate in the linear region of the curve, grain size, and values for the parameter, stress/(grain size)², are summarized in Table 3.3-2. The creep rates in the linear region are plotted in Figure 3.3-4 as a function of the parameter, stress/(grain size)². The deviation of the creep rate of 2BF-204 material from this linear relationship is probably the result of uncertainties in the measurement of the very low total strain.

Fig. 3.3-3—Compressive creep of BeO materials containing 2, 6, 10, and 20 weight percent UO₂ at 1300°C and a stress of 280 kg/cm²

TABLE 3.3-2
COMPOSITION, GRAIN SIZE, CREEP RATE, AND
STRESS/(GRAIN SIZE)² PARAMETER OF COMPRESSIVE CREEP SPECIMENS

Material	UO ₂ Content, wt %	Grain Size, microns	Creep Rate, ^a hr ⁻¹	Stress/(Grain Size) ² , kg/cm ² x 10 ² /(microns) ²
2BF-204	2	28	4 x 10 ⁻⁶	37
6BF-204	6	18	2.5 x 10 ⁻⁵	87
10BF-204	10	11	8 x 10 ⁻⁵	230
20BF-204	20	7	1.5 x 10 ⁻⁴	437

^aCreep rate in the linear region of the curve (over the last 50-hour time interval).

Under the test conditions used, the creep rate of the materials with a high fuel content closely approaches a linear function of the parameter, stress/(grain size)², as predicted by the Nabarro-Herring concept. At the higher fuel contents, the contribution of the plastic fuel phase at the grain boundaries noted in Figure 3.3-2 is not significant after a longer time interval, possibly because of a much greater total strain. As shown in Figure 3.3-3, the creep curve for the 20-percent UO₂ material shows a much higher creep rate in the initial stages, relative to materials with lower fuel contents, and approaches a constant creep rate over a longer time interval.

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Fig. 3.3-4 – Creep rate of compositions of different fuel content as a function of stress and grain size at 1300°C.

THERMAL EXPANSION RESULTS

Thermal expansion measurements were made on BeO-base fuel materials containing 2, 6, 10, 15, and 20 weight percent UO₂ added as the F-204 composition. Details of specimen fabrication and measuring procedures appear in an earlier report.* The results of expansion measurements are given in Figure 3.3-5. The solid line represents the expansion of AOX grade BeO (a non-oriented BeO) calculated from a least-squares equation for the expansion coefficient. The results of this study are basically in agreement with those obtained experimentally for the AOX grade BeO. Two possible exceptions are the 20BF-204 and 2BF-204 compositions. The former probably has a higher thermal expansion due to the increased contribution of the F-204 grain boundary phase which has a greater expansion coefficient than BeO.† The lower expansion of the 2BF-204 composition might be related to the larger grain size (about 25 microns) and consequent preferred orientation of the c-axis of the BeO grains (lower expansion coefficient) parallel to the axis of the specimen. Studies on preferred orientation in BeO have shown that the degree of orientation increases with grain size and that the expansion coefficient decreases in the direction of the preferred orientation.‡

* "High-Temperature Materials Program Progress Report No. 26, Part B," GE-NMPO, GEMP-26B, August 16, 1963, p. 30.

† "Pluto Quarterly Report No. 12," UCRL-6991, July 10, 1962, pp. 32-34.

‡ "Second Annual Report—High-Temperature Materials and Reactor Component Development Program, Volume I—Materials," GE-NMPO, GEMP-177A, February 28, 1963, pp. 137-140.

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Fig. 3.3-5 - Thermal expansion curves of fueled BeO compositions containing 2, 6, 10, 15, and 20 weight percent UO_2 added as F-204

VAPOR PRESSURE STUDIES

As reported previously,* the rhombohedral compound $\text{UO}_2 + x \cdot 3\text{Y}_2\text{O}_3$ is quite stable in air at temperatures as high as 1800°C . The UO_3 vapor pressure of rhombohedral phase is lower than U_3O_8 by several orders of magnitude. Previous data† had shown that rhombohedral compositions were also present in systems of uranium oxide and other rare earth oxides. These two factors suggested a study of representative rhombohedral compositions to assess the effect of size of the rare earth ion on the activity of uranium without a change in structure. The compositions chosen for this study, together with chemical analysis and X-ray diffraction data, are presented in Table 3.3-3. The least-squares fit of the vapor pressure measurements for these compositions is presented in Figure 3.3-6. It is significant to note that the vapor pressure of all compositions at the lower temperatures varies by less than an order of magnitude. At high temperatures, the vapor pressure increases with decreasing ionic radius. At low temperatures the holmium and neodymium compounds

*Ibid., pp. 52-57.

†"First Annual Report - High-Temperature Materials and Reactor Component Development Program, Volume II - Materials," GE-NMPO, GEMP-106B, February 28, 1962, p. 82.

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TABLE 3.3-3
THEORETICAL COMPOSITIONS, CHEMICAL ANALYSES, AND
X-RAY DIFFRACTION RESULTS OF DIFFERENT $\text{UO}_3 \cdot 3\text{R}_2\text{O}_3$ PHASES

Rare Earth Oxide	Rare Earth Ionic Radius, Å ^b	Uranium Oxide Content, ^a wt %		X-Ray Diffraction Results ^c
		Theoretical	Chemical Analysis	
La_2O_3	1.04	22.9	23.0	Essentially 100% Rh I $a = 10.473$, $c = 9.984$
Nd_2O_3	0.99	22.3	22.6	Essentially 100% Rh I $a = 10.254$, $c = 9.748$
Gd_2O_3	0.94	21.1	21.4	Essentially single phase Rh I $a = 10.076$, $c = 9.529$
Y_2O_3	0.88	29.7	27.3	Essentially 100% Rh I $a = 9.934$, $c = 9.364$
Ho_2O_3	0.87	20.4	20.1	Essentially 100% Rh I $a = 9.935$, $c = 9.368$
Lu_2O_3	0.84	19.5	19.2	Major phase Rh I $a = 9.797$, $c = 9.204$ Minor phase Lu_2O_3

^aUranium assumed to exist in the +6 valency state. Accuracy of analysis is ± 0.5 percent of UO_3 content.

^bSeaborg and Katz, "The Actinide Elements," McGraw-Hill, New York, 1954.

^cHexagonal lattice cell parameters are given in Angstrom units.

Fig. 3.3-6—Vapor pressure of UO_3 in rhombohedral rare earth compositions

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deviate from this trend. Since there is more scatter in the vapor pressure measurements at lower temperatures, these deviations may be due to the precision of the measurements. Further studies should be made to understand the effect of ionic radius of rare earth elements on the vapor pressure of these compounds.

FUEL RETENTION STUDIES

Fuel retention studies were carried out at 1370°C, 1510°C, and 1600°C on BeO fueled with 6 weight percent UO_2 added as the F-204 and F-207* fuel compositions. The transpiration technique was used to collect all UO_3 lost from the samples. The results of these tests are shown in Figure 3.3-7. The fuel loss curves from both the 6BF-204 and 6BF-207 at 1370°C and 1510°C are approximately linear with the square root of time. In both cases, however, the initial loss from the 6BF-207 is higher, probably indicating a higher surface loss due to the higher vapor pressure of the F-207 composition. The fuel loss for these two compositions at 1600°C is about the same up to 100 hours. After 100 hours, the 6BF-207 continues to lose fuel at about the same rate as in the first 100 hours, while the 6BF-204 fuel rate decreases appreciably. Loss of UO_2 from 6BF-204 and 6BF-207 is about the same at 1700°C,[†] indicating that the 6BF-204 fuel retention is no longer superior to that of the 6BF-207 at this temperature. Previous testing[‡] of the 6BF-204 composition at 1750°C showed that a liquid phase formed in the fuel-depleted region. This causes a more rapid fuel loss than that from the 6BF-207 composition. The formation of the liquid phase in 6BF-204 at 1750°C is due to the higher Y_2O_3 content of the F-204 fuel composition and the rate of formation is increased as the fuel material becomes depleted in UO_2 , leaving more Y_2O_3 available for liquid formation.

Fig. 3.3-7—Fuel loss of BeO fueled with F-204 and F-207 fuel compositions at 1370°, 1510°, and 1600°C

* F-207 is the composition $45\text{UO}_2-17.3\text{Y}_2\text{O}_3-37.7\text{ZrO}_2$, all in wt %.

[†] "Second Annual Report—High-Temperature Materials and Reactor Component Development Program, Volume II—Materials." GE-NMPO, GEMP-177B, February 28, 1963, p. 82.

[‡]Ibid.

In addition to the kinetic studies described above, an evaluation was completed of 10BF-116* tubes aged at 1200°C and 1370°C for 1000, 5000, and 10,000 hours in dry air. The specimens used were sintered at 1550°C in hydrogen of about 0°C dew point to densities of 98 percent of theoretical. These sintering conditions resulted in an oxygen-deficient fuel phase which accounts for the changes in weight and density observed during oxidation. The purpose of this test was to determine fuel retention capability and physical integrity after extended periods of time at elevated temperatures.

Testing at 1200°C - Assuming UO_2 to be the only component oxidizing, the weight change after 1000 hours showed an increase equivalent to 3.11 percent of the UO_2 present. After 10,000 hours this figure had decreased to 2.74 percent, indicating a loss of about 0.37 percent (chemical analysis showed the loss to be 0.43%). The increase in weight due to oxidation, coupled with an average shrinkage on the bore of 0.0025 centimeter, was reflected in an increase in density of slightly more than 0.013 g/cm³. Other dimensional changes were insignificant. The strength data shown in Table 3.3-4 are about as expected, based on the grain size of the BeO, i. e., strength decreases with increasing grain size.

TABLE 3.3-4

MODULUS-OF-RUPTURE STRENGTH OF 10BF-116 TUBES^a
AT ROOM TEMPERATURE AFTER THERMAL AGING IN AIR

Time At Temperature, ^b hr	Modulus Of Rupture Strength, kg/cm ²						Grain Size, microns	
	1200°C			1370°C			1200°C	1370°C
	Minimum	Maximum	Average	Minimum	Maximum	Average		
None	2200	2690	2430	2200	2690	2430	11	11
1,000	2130	2670	2430	2120	2310	2200	11	11
5,000	2220	2640	2420	1810	2120	1980	11	12
10,000	1810	2910	2290	1900	2110	1980	12	16

^aThe specimens tested were co-extruded 10BF-116 hexagonal external configuration tubes clad on the bore with 0.0076 centimeter of ZrO_2 stabilized with 15 weight percent Y_2O_3 . The 10BF-116 composition was BeO fueled with 10 weight percent UO_2 added as the composition $45\text{UO}_2 - 55\text{Y}_2\text{O}_3$ (wt %).

^bAfter thermal aging in dry air (dew point, ~-65°C) at 1200°C and 1370°C, five specimens (aged at each temperature) were evaluated for modulus of rupture strength. Testing was at room temperature using a 7.62-centimeter span and 4-point loading; rate of ram travel was 0.152 cm/min.

Testing at 1370°C - Results of the 1370°C test were similar to those of the 1200°C test. Oxidation after 1000 hours increased the weight to the equivalent of 2.85 percent of the UO_2 present, again assuming UO_2 to be the only component oxidizing. After 10,000 hours, this figure was reduced to 0.80 percent, a loss of 2.05 percent UO_2 (chemical analysis showed a loss of 1.92 percent). Dimensional changes were insignificant. The strength after 10,000 hours was high compared with the 5,000-hour data and taking into account the increase in grain size; however, the sensitivity of the test method may not be sufficient to reflect this small change in grain size.

PHASE STUDIES IN THE $\text{UO}_2 + x \cdot \text{Y}_2\text{O}_3 - \text{ZrO}_2$ SYSTEM

The phase relationships in the $\text{UO}_2 + x \cdot \text{Y}_2\text{O}_3 - \text{ZrO}_2$ system were studied to determine the limits of the face-centered cubic (FCC) solid solution region. It was established that a single phase FCC solid solution existed in the region bounded by 30 to 55 $\text{UO}_2 + x$, 15 to 55 ZrO_2 , and 10 to 45 Y_2O_3 (in mole percent).[†] Several additional compositions were prepared to define more specifically the solid solution limits. The compositions were prepared by co-precipitation and reacted at 1700°C for 1 hour in air. X-ray diffraction meas-

*BeO fueled with 10 weight percent UO_2 added as the fuel composition $45\text{UO}_2 - 55\text{Y}_2\text{O}_3$, in weight percent. Each tube is clad on the inside surface with 0.0076 centimeter of coextruded ZrO_2 stabilized with 15 weight percent Y_2O_3 .

[†]"High-Temperature Materials Program Progress Report No. 22, Part B," GE-NMPO, GEMP-22B, April 30, 1963, pp. 25-26.

urements established that all of these co-precipitated materials were completely reacted and formed single phase FCC solid solutions. The lattice parameters for the compositions from this study and from the previous study are shown in the ternary phase diagram in Figure 3.3-8. The composition limits of the single phase (FCC) region have thus been shown to extend to at least 15 to 75 UO_{2+x} (where x ranges from 0.133 to 1.0), 15 to 65 ZrO_2 , and 10 to 55 Y_2O_3 (all in mole percent).

Fig. 3.3-8 - Phase relations in UO_{2+x} - Y_2O_3 - ZrO_2 system

SUMMARY AND CONCLUSIONS

The creep rates of BeO fueled with the F-204 composition to UO_2 contents ranging from 2 to 20 weight percent were shown to be linear with the parameter, $\text{stress}/(\text{grain size})^2$, at grain sizes up to 50 microns. The thermal expansions of these materials are in good agreement with that of unfueled BeO. Fuel loss experiments from several stabilized UO_2 -BeO fuel materials show that the fuel loss is linear with the square root of time, after equilibrium is attained, indicating a diffusion-controlled process.

Phase studies in air at temperatures from 1700°C to 1850°C have extended the composition limits of the single phase face-centered cubic region to at least 15 to 75 UO_{2+x} (where x ranges from 0.133 to 1.0), 15 to 65 ZrO_2 , and 10 to 55 Y_2O_3 (all in mole percent).

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The UO_3 vapor pressures for the rhombohedral compounds $\text{UO}_3 \cdot 3\text{R}_2\text{O}_3$, where R is the rare earth element, increases with decreasing ionic radius of the rare earth. The $\text{UO}_3 \cdot 3\text{La}_2\text{O}_3$ compound has the lowest UO_3 pressure in the series over the temperature regions from 1300° to 1600°C.

A topical report is being written on this terminated task.

3.4 FISSION PRODUCT MIGRATION IN SOLIDS (57067)

This job terminated at the end of Fiscal Year 1963; however, a part of the work, diffusion studies on ion-bombarded oxides, was continued under "Fission Gas Diffusion in Unfueled Ceramic Materials," Job 57069, and that portion done under Job 57067 is summarized in Section 4 of GEMP-270A.

The objective of this program is to study fission gas transport processes from selected ceramic systems and to advance the understanding of fission gas release from ceramic fuel elements and ceramic materials in general. The work is divided into three major related phases to obtain information useful in understanding both the specific and the broad aspects of fission product release in ceramic systems. These phases are:

1. Diffusion Studies on BeO-Dispersed Oxide Fuel Elements
2. Xe^{133} Diffusion Studies From Selected $\text{UO}_{2+x} \cdot \text{Y}_2\text{O}_3$ Compositions*
3. Diffusion Studies on Ion-Bombarded Oxides

The work on diffusion of fission products from BeO-dispersed oxide fuel elements and diffusion from $\text{UO}_{2+x} \cdot \text{Y}_2\text{O}_3$ compositions is being brought to a logical conclusion under "Burnup Capabilities of Y_2O_3 -Stabilized UO_2 and Stabilized Fuel-BeO Matrix Materials" (57068). That portion of the work under Job 57067 pertaining to these two subjects and the work continued under Job 57068 are summarized herein.

The kinetic release data† for I^{131} from $\text{BeO} \cdot [\text{UO}_2 \cdot 1.5\text{Y}_2\text{O}_3]$ samples in an air atmosphere at 1400°C and 1500°C indicated that there was an initial release, which was not necessarily comparable from test to test, followed by release which was diffusion controlled and which was comparable for all experiments at a given temperature. At 1500°C, approximately 0.4 percent of the total iodine inventory was released by a diffusion process in 100 hours. The initial release appeared to come from the surface-exposed fuel particles. The kinetics of Kr^{85} release from $\text{BeO} \cdot [\text{UO}_2 \cdot 1.8\text{Y}_2\text{O}_3]$ samples in a vacuum were similar to those obtained for I^{131} . The release of Kr^{85} had an apparent activation energy of 65 kcal/mole between 1000°C and 1350°C.†

DIFFUSION STUDIES ON BeO-DISPERSED OXIDE FUEL ELEMENTS

The diffusion of fission products from BeO-dispersed oxide fuel elements can have one of several rate-limiting steps, i. e., diffusion in the fuel phase, diffusion in the BeO grains, and grain boundary diffusion. To identify the release processes, the change in surface fuel concentration with time; the effects of temperature, microstructure, and fuel phase composition on I^{131} release; and more data on the effects of temperature on Kr^{85} release were obtained by a post-irradiation heat treatment. In addition, data on the release of various krypton and xenon isotopes were obtained from several dynamic in-pile tests in the LITR at Oak Ridge; these data permitted a comparison of the release kinetics for two different fuel loadings in BeO.

*Item 2 was formerly reported as "Diffusion Studies On Anion-Deficient $\text{UO}_2\text{-Y}_2\text{O}_3$ Compositions."

†"Second Annual Report—High-Temperature Materials and Reactor Component Development Programs, Vol. II—Materials," GE-NMPO, GEMP-177B, February 28, 1963, pp. 96–99.

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Materials

The materials used in the diffusion experiments were tubular samples of BeO-dispersed oxide fuel material in excess of 98.5 percent of theoretical density. The composition, designation, and microstructure of these samples are summarized in Table 3.4-1. To facilitate the subsequent discussion, the sample designations shown in the table will be used.

TABLE 3.4-1
SUMMARY OF MATERIALS AND MICROSTRUCTURE DETAILS
USED IN DIFFUSION STUDIES

Designation ^a	Composition	Average BeO Grain Size, microns	Detectable Eutectic Phase ^b In Grain Boundaries
6BF-48	BeO-[UO ₂ ·1.8 Y ₂ O ₃]	50-60	Yes
6BF-116	BeO-[UO ₂ ·1.5 Y ₂ O ₃]	50-60	Yes
8BF-116	BeO-[UO ₂ ·1.5 Y ₂ O ₃]	10-15	No
6BF-204 ^c	BeO-[UO ₂ ·Y ₂ O ₃ ·ZrO ₂]	10-15	No

^aThe number preceding the BF notation indicates the fuel loading in weight percent UO₂.

^bWhen samples containing the UO₂·Y₂O₃ fuel phase are sintered above the BeO·Y₂O₃ eutectic temperature of 1580°C, a large BeO grain size results and a eutectic phase is evident in the grain boundaries. If the samples are sintered at 1550°C, below the eutectic temperature, a small grain size results and no eutectic phase is evident in the grain boundaries.

^cPreparation of this material was summarized under Job 57068 (section 3.1 of this report).

Comparison of Iodine Release with Surface Fuel Concentration

Segments of fuel elements were heated isothermally at 1400°C and 1500°C in flowing dry air (-65°C average dewpoint) and the changes in weight, alpha count rate, and gamma count rate were measured periodically. The fuel loss was also measured by a transpiration technique and found to agree within the limits of detection with the weight changes and the gamma count rate changes. The alpha count rate is a measure of the average-surface or near-the-surface fuel concentration and can indicate the amount of evaporation of fuel from the surface resulting from the various heat treatments.

For the fuel element (6BF-116) sintered above the eutectic temperature, the alpha count rate showed a rapid decrease initially, remained relatively constant for a period, and then decreased again before reaching a steady state value after 10 hours at 1500°C. This behavior is shown in Figure 3.4-1 for two different specimens. The data from both specimens showed similar curve shapes, although the magnitude of the count rate change was different. The surface fuel particles for fuel elements sintered in the presence of the eutectic were found to consist of three fuel phases. On heating in air, the three phases recombined to form the stable UO_{2+x}·3Y₂O₃ compound but not without a rapid volatilization of urania from the surface particles. The actual process during equilibration is complex and is believed to be responsible for the intermediate inflection in the alpha count rate curve.

The I¹³¹ release from the 6BF-116 fuel element at 1500°C is also shown in Figure 3.4-1 along with fuel loss data obtained from a transpiration experiment. It is evident that the magnitude of the I¹³¹ release in the early portions of the test period (<400 min) ranges from 0.2 to 5 percent (note change in scale). However, the specimens which exceeded 0.5 percent release in this time period were reheat treated in a dry hydrogen atmosphere at 1540°C or 1590°C for 5 hours and cooled rapidly after sintering. The fuel specimens which were used in the as-sintered condition or reheat treated in air at 1620°C for 8.7 hours gave consistently lower release rates, after short initial bursts of about 0.05 to 0.1 percent.

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Fig. 3.4-1 - Iodine-131 release and surface fuel loss at 1500°C from 6BF-116 ceramic fuel elements

A comparison of these data indicates that the iodine release is not controlled or significantly influenced by loss of fuel or phase changes in the surface fuel. However, Xe¹³³ release measurements from powder samples of the F-116 fuel phase indicate that the release at 1500°C from fuel particles which intersect the BeO surface would be very rapid, so some rapid iodine release would be expected. The release from the samples which were reheat treated in dry hydrogen is extremely rapid in the early stages (1 to 3% in 1 hour) and suggests that some cracking or grain boundary separation occurred as a result of the pretreatment. The amount of fuel which connects with the surface will depend on the degree of grain boundary separation or cracking and hence can account for the widely varying magnitude of the initial release by direct release of iodine from varying amounts of exposed fuel. Similar results were obtained at 1400°C.

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No correlation of I^{131} release kinetics with surface fuel loss was apparent from a similar comparison of data for the 8BF-116 samples. Additional experiments are planned to determine if grain boundary separation or cracks can account for the initial release kinetics of I^{131} .

Iodine-131 Release Experiments

Measurements of I^{131} released from the irradiated samples using a post-irradiation heat treatment were made by continuously monitoring (using gamma ray spectrometry) a liquid absorption trap (downstream from the heated sample) using dry air as the carrier gas. Radiochemical techniques were employed to determine the total fraction of the I^{131} inventory released during each experiment in order to convert measured counting data to the fraction released.* An addition to the apparatus was made to obtain Xe^{133} release kinetics as well.† Although a reliable total release for Xe^{133} has not been obtained because of the lack of a suitable counting standard, the data indicated that curve shapes were quite similar to those obtained for the I^{131} release.

Experiments were run at 1400°C and 1500°C on 6BF-116 and 8BF-116 samples and at 1400°C, 1500°C, and 1600°C on samples of 6BF-204 to determine the effects of different microstructure and different fuel phase composition on I^{131} release kinetics. A comparison of some of the data obtained at 1400°C and 1500°C from these samples is shown in Figures 3.4-2 and 3.4-3.

The data in the figures indicate that release due to diffusion is very low for the 6BF-116 and 6BF-204 samples. Even at 1600°C, the diffusion-controlled release from a 6BF-204 sample only amounted to 0.4 to 0.5 percent release in approximately 100 hours. The magnitude of release from the 8BF-116 sample at 1500°C indicates that iodine is coming from

Fig. 3.4-2—Comparison of I^{131} release kinetics at 1400°C for samples with different microstructure and fuel phase composition

*"First Annual Report—High-Temperature Materials and Reactor Component Development Programs, Vol. II—Materials," GE-NMPO, GEMP-106B, February 28, 1962, p. 140.

†"High-Temperature Materials Program Progress Report No. 30, Part B," GE-NMPO, GEMP-30B, December 31, 1963, pp. 31-33.

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Fig. 3.4-3 – Comparison of I^{131} release kinetics at 1500°C for samples with different microstructure and fuel phase composition

deeper within the body. However, the magnitude of release for the test time indicated is largely determined by a higher initial release rate which persists for approximately 40 hours. Beyond this time, a lower rate characterizes the iodine release.

The release rates in the experiments shown in Figures 3.4-2 and 3.4-3 were followed for times up to 250 hours. One sample was pretreated in air at the test temperature for 2177 hours before irradiation. It is not certain whether a constant slope is present even after this period of heat treatment. Even longer times may be required to establish the true rate of release from the body after surface damage has been annealed and equilibrium has been obtained within the body.

Krypton-85 Release Experiments

The studies to determine post-irradiation release kinetics of Kr^{85} from the 6BF-48 fuel element can be summarized as follows.

Measurements of Kr^{85} release were made in vacuum as a function of temperature and time between 1000° and 1400°C for durations up to 365 hours at temperature. The largest release fraction observed was 0.11; however, in most runs the release fraction was 0.01 or less.

The kinetic behavior of the observed Kr^{85} release was analyzed by plotting the release fraction versus the square root of time at temperature. The various isothermal curves fall into two groups. Those obtained at or below 1350°C were characterized by an initial rapid rate of release which decreased, in from 4 to 50 hours, to a rate which was constant with the square root of time. The same initial behavior was noted in runs above 1350°C , but after a short time the release rate began to increase. From the temperature dependence of the diffusion-controlled linear portions of the curves, an activation energy of about 130 kcal/mole was obtained. This value is different from that indicated earlier because of additional data, and is in substantial agreement with those obtained from I^{131} release and Xe^{133} release from similar specimens as will be discussed under temperature dependence of the release rate.

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The initial Kr^{85} release was analyzed separately by using the release during the first hour to approximate the initial slope of the fraction released versus square root of time curve and determining its temperature dependence. An activation energy of about 60 kcal/mole was obtained. Since release from the fuel phase is expected to dominate the release kinetics for short times, as indicated earlier, it appears that the 60 kcal/mole activation energy may characterize diffusion from the surface fuel.

Temperature Dependence of the Release Rate

The logarithms of the square of the release rate of Kr^{85} , Xe^{133} , and I^{131} from the 6BF-116 fuel element were combined in Figure 3.4-4 and plotted as a function of the reciprocal absolute temperature. In all cases the final slope of the release versus square root of time curve was used. The Kr^{85} and Xe^{133} * data were obtained in vacuum and the I^{131} data were obtained in air. The wide scatter in the data precludes any precise determination of the activation energies; however, several observations are evident.

1. The activation energies for I^{131} , Kr^{85} , and Xe^{133} from the 6BF-116 fuel element appear to be nearly the same and are in the vicinity of 135 kcal/mole.
2. The temperature dependence of the I^{131} release rate for the solid-state sintered fuel element (8BF-116) does not appear to differ significantly from that of the liquid-state sintered fuel element (6BF-116) at temperatures to 1500°C but the results for the 6BF-204 composition to 1600°C indicate that the activation energy for diffusion for the 6BF-204 fuel element may be significantly lower.
3. At 1600°C , the 6BF-116 fuel elements show a large increase in the release rate of I^{131} as compared to the 6BF-204 fuel element. This is undoubtedly the result of the presence of a liquid phase which forms in the 6BF-116 fuel element above 1580°C but does not appear in the 6BF-204 until temperatures are much higher ($\sim 1750^{\circ}\text{C}$).

The magnitude of the total release obtained at 1500°C was 1 percent or less and 0.5 percent or less at 1400°C in most of the experiments. Release from deep within the body was not attained, which made identification of the rate controlling process difficult. Nevertheless, the data in Figure 3.4-4 suggest that the same diffusion mechanism may be rate-controlling for I^{131} , Xe^{133} , and Kr^{85} diffusion from the composite body regardless of microstructure. Activation energies for diffusion of these isotopes in the fuel phase itself are generally around 70 to 80 kcal/mole which would suggest that either grain-boundary diffusion or diffusion in the BeO grains is rate-controlling for the composite body.

In-Pile Measurement of Fission Product Release

Fission product release data from two dynamic in-pile tests and the data from a test run during the ANP program were compared.[†] The pertinent aspects of the materials tested, the test conditions, and the results are given in Table 3.4-2. For the tubes containing 6.5 volume percent fuel (6 weight percent UO_2), there was on the average 10 to 15 microns of BeO between the fuel particles. For the tubes containing 25 volume percent fuel phase (20 weight percent UO_2), the fuel phase was virtually continuous.

The results noted in the table indicated no observable fission product release by a diffusion process for several hundred to approximately 1500 hours at temperatures of 1400°C and 1260°C , respectively, when the fueled particles were surrounded by BeO. However, release by a diffusion process was observed in 100 to 200 hours at 1330° to 1370°C when

*D. F. Toner and J. L. Scott, "The Release of Xe-133 from a Stabilized BeO- UO_2 Fuel," ORNL, ORNL-CP 62-3-9, March 2, 1962.

†P. K. Conn and H. C. Brassfield, "Fission Product Retention Potential of Oxide Coated Fuel Particles Based on BeO-Dispersed Oxide Ceramic Fuel Element Data," GE-NMPO, TM 63-6-7, June 1963, pp. 3-10.

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Fig. 3.4-4 – Temperature dependence of release of I¹³¹, Kr⁸⁵, and Xe¹³³ from irradiated dispersed oxide ceramic fuel elements

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TABLE 3. 4-2
COMPARISON OF FISSION PRODUCT RELEASE FROM SEVERAL
DYNAMIC IN-PILE TESTS

Material	Fuel Phase, vol %	Test Conditions ^a	Results
6BF-199 ^b	6.5	291 hours at 1420°C	Recoil release
6BF-204	6.5	1475 hours at 1260°C	Recoil release
20BF-204Gd ^{c, d}	25	Below 1250°C	Recoil release
		470 hours at 1330°-1370°C	Recoil release and release by diffusion
		Below 1200°C ^e	Recoil release

^aThe temperatures noted are the average maximum indicated test temperatures except where otherwise noted (about one-third of the tube was at the given temperature).

^bThe composition of these tubes was BeO-[UO₂·1.2Y₂O₃·1.2ZrO₂].

^cOne weight percent gadolinia was added to the fuel phase as a burnable poison.

^dThe test operated 1193 hours at different temperatures.

^eOperation subsequent to 1330° to 1370°C operation.

the fuel particles virtually formed a continuous phase in the BeO matrix. This comparison indicates that the BeO retains fission products to a greater degree than the fuel phase at high temperatures and that fission product loss from the fuel phase is more rapid than from the composite body.

XENON-133 DIFFUSION FROM SELECTED UO_{2+x}·Y₂O₃ COMPOSITIONS

The purpose of this study is (1) to obtain fundamental information on the effect of anion vacancies on the diffusion of Xe¹³³ in various (UO_{2+x}·Y₂O₃) compositions and (2) to obtain diffusion information on the fuel compositions used in the BeO fuel elements. Two compositions were investigated, UO₂·3·1.5Y₂O₃ and 4UO₂·3·Y₂O₃; other compositions were prepared for study. The composition UO₂·3·1.5Y₂O₃ is the same as that used in the BeO-[UO₂·1.5Y₂O₃], and has essentially the same crystallographic phases present that are in the as-sintered material which was sintered below the eutectic temperature.

UO₂·3·1.5Y₂O₃ (F-116)

The analysis of results of the kinetic study of Xe¹³³ release from irradiated specimens of the anion-deficient UO₂·3·1.5Y₂O₃ composition (F-116) in the temperature range of 900° to 1400°C was reported previously.* A brief summary of the experiments and results obtained is presented here.

The powder specimens used in the study consisted predominantly of a rhombohedral phase plus about 10 to 15 percent of a body-centered cubic phase. Equivalent particle diameter, determined by BET-krypton adsorption for the various powder samples, varied from 2.7 to 37 microns. A sample of the powder, after the short (1 to 12 hours) irradiations, was fused in Li₂B₄O₇ at 720°C; the amount of evolved Xe¹³³ was used to compute the Xe¹³³ inventory per gram for the analysis of the kinetic data in terms of fractional release.

The kinetic data were obtained by isothermally heating the powder in vacuum at temperatures between 900° and 1400°C. Deviations from ideal diffusion kinetics (straight line passing through the origin) were manifested by an initial rapid rate of release followed by a

*"High-Temperature Materials Program Progress Report No. 28, Part B," GE-NMPO, GEMP-28B, November 11, 1963, pp. 29-32.

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linear relationship with the square root of time. Analysis of the temperature dependence of the diffusion coefficients calculated from the kinetic data resulted in an activation energy of 85 kcal/mole in the temperature range studied. For the temperature dependence analysis, it was assumed that the initial rapid release was characteristic of the smallest equivalent particle size measured, and the later release, of the larger particle size; two values of D were calculated from the data for each temperature. The agreement was normally within one order of magnitude. The change in particle size necessary to bring the values at each temperature into coincidence was a factor of 6 or less, which is within the observed variation of a factor of 14 in equivalent particle diameter.

These results indicated that the release of Xe^{133} from irradiated $\text{UO}_2 \cdot 3 \cdot 1.5\text{Y}_2\text{O}_3$ powder occurs by a solid state diffusion process with an activation energy of about 85 kcal/mole which may be contrasted with the characteristic activation energy of 135 kcal/mole when the fuel particles are dispersed in BeO. The deviation from ideal diffusion kinetics observed in the early portion of the runs is believed to result from the range of particle sizes in the powder.

$4\text{UO}_2 \cdot 3 \cdot \text{Y}_2\text{O}_3$

Post-irradiation Xe^{133} release measurements were begun on $4\text{UO}_2 \cdot 3 \cdot 1.5\text{Y}_2\text{O}_3$ powder whose oxygen-to-metal ratio of 2.04 is very near to that of the ideal fluorite lattice (2.00) in which theoretically no excess anion vacancies exist. The preparation, pre-irradiation conditioning, and irradiation of the powder was previously reported.* Kinetic data were obtained at approximately 900°, 970°, and 1150°C; experiments at other temperatures will be made plus an experimental determination of the Xe^{133} inventory so that the results may be interpreted on a fractional release basis.

SUMMARY AND CONCLUSIONS

The release of I^{131} , Kr^{85} , and Xe^{133} from BeO-dispersed oxide fuel elements containing 6 to 8 weight percent UO_2 (6.5 to 9 volume percent fuel phase) is diffusion controlled and has an apparent activation energy of approximately 135 kcal/mole. The magnitude of release by the diffusion process is less than 0.5 percent after 100 hours at 1500°C. While coming to equilibrium at temperatures of 1400°C and 1500°C, there is an initial release of I^{131} which appears to be that residing within the surface-exposed fuel particles; this release does not appear to be significantly affected by loss of UO_2 or phase changes which occur in the surface-exposed fuel particles.

The release of Xe^{133} from powder samples of the fuel phase used as the dispersion in 6BF- and 8BF-116 is also diffusion controlled and has an activation energy of approximately 85 kcal/mole.

Fission product release data obtained from dynamic in-pile tests on BF-204 fuel elements containing either 6.5 volume percent fuel phase (the fuel particles are surrounded by BeO) and 25 volume percent fuel phase (the fuel phase is virtually continuous) indicated that the release is higher when the fuel phase is continuous. BeO bodies containing non-continuous dispersions of fuel are promising materials for retaining fission products at high temperature.

*"High-Temperature Materials Program Progress Report No. 30, Part B," GE-NMPO, GEMP-30B, December 31, 1963, pp. 33-34.

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4. OTHER HIGH-TEMPERATURE NUCLEAR MATERIALS RESEARCH

4.1 REACTOR CONTROLS, REFLECTOR, AND SHIELD MATERIALS RESEARCH (57002)

The objective of this task is the development of a materials science and technology which will further the rapid development of new or improved reactor components for high-temperature nuclear reactors.

METAL HYDRIDE STUDIES

This work consists of a metallurgical development and evaluation program to develop improved fabrication techniques, increase the hydrogen content per unit weight, and evaluate the engineering properties of hydrided materials.

Clad Hydrided Yttrium Alloy

The second annual report* outlined the characteristics of clad hydrided yttrium alloys after bench testing at 870° to 1040°C for 6000 hours and after in-pile tests at 690° to 700°C for 1950 hours (LTYH_x-1) and at 1000°C for 2450 hours (LTYH_x-2). These specimens were Y - 5Cr (wt %),[†] flame-sprayed with 0.007-centimeter chromium, hydrided to an N_H of 5.1 to 5.3 (approximately 2.0 percent hydrogen), and clad with 0.040 centimeter of Fe - 20Cr - 4.5Al.

The equilibrium hydrogen vapor pressures at high temperatures of yttrium hydride are the lowest of any known hydride. This may permit operating temperatures of at least 200°C higher than other hydrides. However, long-time thermal stability and clad stability at these higher temperatures must be demonstrated. Tests are being conducted to evaluate these characteristics.

Several 10,000- to 11,000-hour thermal stability tests were completed at 1040°, 980°, and 950°C. A summary of the test data is presented in Table 4.1-1. Figure 4.1-1 shows the core condition of one of these specimens after 10,000 hours at 950°C. The limited core cracking shown in Figure 4.1-1b was apparent in all specimens after 10,000 hours and is attributed in part to thermal cycling; the specimens were submitted to numerous, relatively severe thermal cycles during the course of the test. The cracking, however, has had no effect on the dimensional stability of the specimens. No core cracks were apparent in the first 5000 hours of testing. Cladding blisters occurred in three of the four specimens tested at 1040°C and three of the five specimens at 950°C, which had experienced a furnace excursion to temperatures appreciably greater than 1000°C. No other blistering has been noted at temperatures below 1000°C. The cladding blisters

*"Second Annual Report - High-Temperature Materials and Reactor Component Development Programs, Volume II - Materials," GE-NMPO, GE-MP-177B, February 28, 1963, pp 240-246

[†]All compositions are in weight percent unless otherwise noted.

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TABLE 4.1-1
YTTRIUM HYDRIDE MODERATOR THERMAL STABILITY TEST SUMMARY

Specimen Number	Test Temperature, °C	Time At Temperature, hr	Cladding Condition	Bond Condition Ultrasonic	Core Condition X-Ray	Length		Width		Thickness		Weight	
						Original, cm	Change, %	Original, cm	Change, %	Original, cm	Change, %	Original, g	Change, %
Bench Tests													
131	1040	10,195	Good - no blisters	One edge unbonded	Cracks	8.616	0.65	2.045	0.37	1.067	0.71	85.506	-0.16
119	1040	10,195	Two edge blisters	Unbonded areas on face	Cracks	8.626	0.53	2.042	0.37	1.067	0.71	85.256	-0.19
128	1040	11,011	One edge blister	Small unbonded areas	Cracks	8.585	0.65	2.068	0.10	1.082	2.13	84.206	-0.068
184	1040	11,011	Blister on all surfaces	All sides unbonded	Cracks	8.606	1.06	2.062	0.15	1.072	0.71	85.400	-0.064
151	980	10,140	Good - no blisters	Bonded	Cracks	8.623	0.62	2.068	-0.86	1.082	-0.94	84.775	-0.28
157	980	10,140	Good - no blisters	Bonded	Cracks	8.623	0.21	2.055	-0.25	1.085	-0.47	85.644	-0.28
127	980	11,006	Good - no blisters	Unbonded spots on face	Cracks	8.519	0.00	2.062	-0.58	1.080	-0.71	83.718	-0.200
109	950 ^a	10,000	Good - no blisters	Bonded	Cracks	8.623	0.80	2.045	0.50	1.067	0.48	85.501	-0.08
112	950 ^a	10,000	One edge blister	One edge unbonded	Cracks	8.606	0.83	2.047	0.37	1.062	1.44	85.104	-0.04
158	950 ^a	10,000	Good - no blisters	Bonded	Cracks	8.573	0.74	2.057	0.12	1.077	0.00	85.031	-0.31
125	950 ^a	11,016	One edge blister	Two unbonded spots	Cracks	8.611	0.94	2.075	0.61	1.087	0.00	86.863	-0.15
126	950 ^a	11,016	One edge blister	Unbonded edge	Cracks	8.636	0.18	2.063	0.25	1.080	-1.41	84.025	-0.13
Fourth In-Pile Test (LTYH _X -4)													
137	900	5,150	Good - no blisters	Bonded	Excellent	8.646	-0.15	2.042	-0.24	1.074	-0.19	86.105	0.00
161	900	5,150	Good - no blisters	Bonded	Excellent	8.616	-0.59	2.042	0.00	1.072	-0.28	85.160	-0.02
175	900	5,150	Good - no blisters	Bonded	Excellent	8.639	-0.15	2.045	0.00	1.069	0.00	85.354	+0.01
191	900	5,150	Good - no blisters	Bonded except for one end	Excellent	8.636	-0.42	2.047	0.00	1.064	0.00	84.914	0.000

^aSpecimens experienced a temperature excursion to approximately 1200°C as a result of a furnace instrumentation failure.

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Neg. 3390

250 X

Neg. 3428

75 X

a. Center section of core showing two-phase microstructure of YH_x and Cr

b. Type of cracking noted in the core

Neg. 3427

5 X

Neg. 3392

250 X

c. Cross section showing crack pattern (contrast enhanced by shadow techniques). Crack noted in the specimen mount suggests that some cracking was caused during sample preparation.

d. Core-to-clad bond area (core at left) showing condition of bond and Cr flame-sprayed interface

Fig. 4.1-1—Hydrided Y-5Cr (wt %) specimen number 112 after 10,000 hours at 950°C. Note: The hydrogen retention of this specimen was a nominal 90% at the end of the test period.

appeared to have little effect on hydrogen retention. One specimen with cladding blisters was destructively analyzed for hydrogen after 10,000 hours at 950°C; it had retained more than 90 percent of the original hydrogen. None of the specimens showed a significant weight change during the test. Figure 4.1-2 is a photograph of six of the bench-test specimens after 10,000 hours of testing.

Two in-pile tests had been completed at the end of CY-63, and two additional tests (LTYH_x-3 and LTYH_x-4) were initiated during this year. The specimens and cartridge designs were identical to the two previous tests.* One test (LTYH_x-4) was completed. It was operated in air at 900°C for 5100 hours for an estimated thermal neutron exposure of 1.3×10^{20} nvt. The four specimens in this cartridge have completed the early phases of a hot laboratory examination, and no evidence of distortion, dimensional or weight instability, or cladding blisters was found. The cladding-to-core bond of all specimens

* "Second Annual Report—High-Temperature Materials and Reactor Component Development Programs, Volume II—Materials," GE-NMPO, GEMP-177B, February 28, 1963, p. 241.

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Fig. 4.1-2—Hydrided Y-5Cr (wt %) test specimens clad with Fe-20Cr-4.5Al (wt %) after 10,000 hours in air at the stated temperatures

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was intact, as determined by ultrasonic inspection, except for one end of one specimen. No core cracking was noted by X-rays taken through lead with a Van de Graaff electrostatic accelerator. However, resolution, as determined with cracked standards, was marginal. A summary of these tests is shown in Table 4.1-1. Figure 4.1-3 shows the four specimens after completion of the test. The third in-pile test (LTYH_x-3) is scheduled to run at 925°C for 10,000 hours to an estimated thermal neutron exposure of 5×10^{20} nvt. To date, this test has operated at 925°C to 940°C for 6800 hours for an estimated thermal neutron exposure of 3.4×10^{20} nvt. The data to date clearly demonstrate the potential of clad yttrium hydride as a useful, high-performance reactor material for long-term service.

Fig. 4.1-3—LTYH_x-4 test specimens after 5100 hours at 900°C and a thermal neutron exposure of 1.3×10^{20} nvt (Neg. R17783)

The thermal stability and in-pile test results on the hydrided Y-Cr moderator material show this material to have excellent potential use in high-temperature reactors. The outstanding dimensional and weight stability characteristics together with the hydrogen-retention properties of this material over a 10,000-hour test period represent the first successful long-time operating life demonstration of metal hydrides at temperatures in the 1000°C range.

A nondestructive technique had been devised* to determine the hydrogen content of test specimens. This technique relates the hydrogen content to the ratio of neutrons, from a collimated beam, scattered by the specimens to those attenuated by the specimen. The same method can be used to measure the hydrogen content of irradiated specimens if the secondary gamma radiation response can be minimized, or discriminated and filtered. The equipment is being modified to provide this capability. The neutron flux in the beam was increased and solid-state detectors with low gamma sensitivity were substituted. The new detector characteristics required a change in circuitry which is being proof-tested.

*"First Annual Report—High-Temperature Materials and Reactor Component Development Programs, Volume II—Materials," GE-NMPO, GEMP-106A, February 28, 1962, p. 37.

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Hydriding Procedure Development

The controlled introduction of hydrogen into a metal lattice requires an extremely well-defined process if crack-free and dimensionally stable structures containing high percentage of hydrogen are to be produced. The hydriding process involves long-time exposures at elevated temperatures during which grain growth may take place. Grain growth of the hydride is somewhat anisotropic and planes of weakness are frequently produced in grain-boundary areas of specimens possessing a coarse, highly oriented grain structure. Methods of reducing initial grain size, inhibiting subsequent growth, and maintaining randomness of grain orientation by adding a specially selected second phase and by prehydride working such as forging were previously described.* This work clearly demonstrated the advantages of fine-grain, controlled microstructure in hydrided zirconium material. However, independent of the metallurgical structure, the hydriding process still required almost continuous surveillance during periods of maximum hydrogen absorption. Unless this process was properly monitored and controlled, the required hydrogen content of specimens was above or below specification and the grain size tended to shift slightly from the optimum.

Partial resolution of this problem was attained through the development of a special hydriding cycle previously described† in which programmed temperature reductions were interrupted during periods of higher than average absorption rates, and hydrogen concentration gradients within the specimen were minimized through the use of a hydrogen throttling valve. Examination of previous hydriding runs indicated that if the ratio of work-load size to furnace volume were large and the inlet hydrogen flow restricted, furnace pressure was reduced during periods of high-hydrogen absorption. This pressure reduction was large enough to automatically interrupt the temperature reduction cycle. Therefore, a pressure-sensitive on-off switch to control the constant temperature holding periods, a time - temperature furnace programmer, and a flow restrictor valve were incorporated in the hydriding process. This has made possible an automatic, self-regulating hydriding process cycle. A block chart and a schematic diagram of the temperature programmer - pressure switch portion are shown in Figure 4.1-4.

A series of hydriding runs was made using the automated equipment. Each operation imposed some new demand, such as a larger specimen cross section for a given type of metallurgical prehydride processing, a higher hydrogen content for a large number of specimens, or the hydriding of a significantly different composition (HfH_x studies). Each of these runs was successful and included:

1. A 1.0 by 2.0 by 8.9 centimeter zirconium specimen was hydrided to N_H 7.09 (2.11 wt % hydrogen, see Figure 4.1-5), and a 1.25-centimeter-diameter Zr - 10U specimen was hydrided to N_H 6.99 (see Figure 4.1-6). These specimens are in excellent condition and represent an exceptionally high hydrogen content in a sound, crack-free zirconium hydride sample.
2. Ten Zr - 10U specimens containing 0.07 to 0.35 weight percent carbon were hydrided to N_H 6.0.
3. A hafnium rod approximately 1.25 centimeters in diameter was hydrided to N_H 6.0 (density, 11.5 g/cm³; hydrogen 0.88 wt %). The as-hydrided specimen was sound and dimensionally stable (see Figure 4.1-6).
4. Twenty-five hydrided titanium rods were processed for a critical reactor experiment. These rods were approximately 0.317 centimeter in diameter and 15.24 centimeters in length. The titanium specimens were hydrided simultaneously to an average N_H of 8.61 (range 8.45 to 8.75; standard deviation, σ , = 0.074 N_H units). The hydrogen content data are shown in Table 4.1-2.

* G. R. Van Houten, "Effect of Certain Processing Variables on Physical Properties of High Hydrogen Density (N_H 6.0-6.6) Zirconium Hydride," GE-ANPD, APEX-679, April 1961.

† "High-Temperature Materials Program Progress Report No. 13, Part B," GE-NMPO, GEMP-13B, July 31, 1962, p. 60.

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Fig. 4.1-4 - Programmer-pressure switch portion of the new automated hydriding controller

Fig. 4.1-5 - Sound, crack-free hydrided-zirconium specimen hydrided with the newly developed automatic time-temperature programmer and special pressure switch interrupter (hydrogen content - 2.11%, density - 5.62 g/cm³, and N_H - 7.09)

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Zr-10U
HYDROGEN CONTENT, 1.93%
DENSITY, 6.0 g/cc
 N_H , 6.99

Hf
HYDROGEN CONTENT, 0.825%
DENSITY, 11.5 g/cc
 N_H , 6.0

Fig. 4.1-6— Sound zirconium and hafnium specimens hydrided together on a single run (Neg. P63 4-21)

TABLE 4.1-2
UNIFORMITY OF HYDROGEN CONTENT IN
TITANIUM SAMPLES FROM A TYPICAL AUTOMATED RUN

Sample	Weight Before Hydriding, g	Weight Gain, g	Hydrogen Content, %	Density, g/cm ³	N_H
1	4.36	0.1700	3.752	3.806	8.54
2	4.35	0.1693	3.743	3.778	8.46
3	4.26	0.1668	3.761	3.819	8.75
4	4.31	0.1662	3.710	3.836	8.51
5	4.30	0.1699	3.793	3.820	8.67
6	4.37	0.1707	3.753	3.819	8.57
7	4.35	0.1720	3.790	3.819	8.67
8	4.25	0.1675	3.790	3.822	8.66
9	4.32	0.1697	3.776	3.818	8.62
10	4.33	0.1719	3.816	3.822	8.72
11	4.30	0.1683	3.759	3.819	8.59
12	4.31	0.1680	3.750	3.819	8.51
13	4.30	0.1708	3.766	3.824	8.61
14	4.30	0.1674	3.745	3.818	8.55
15	4.28	0.1682	3.775	3.821	8.63
16	4.35	-	-	3.817	-
17	4.33	0.1700	3.775	3.819	8.62
18	4.34	0.1713	3.792	3.821	8.66
19	4.36	0.1722	3.798	3.761	8.54
20	4.34	0.1711	3.792	3.819	8.66
21	4.34	0.1709	3.789	3.766	8.54
22	4.34	0.1713	3.796	3.823	8.68
23	4.29	0.1691	3.789	3.821	8.66
24	4.33	0.1715	3.802	3.824	8.70
25	4.35	0.1687	3.732	3.821	8.53

^aTitanium rods swaged from 0.465 to 0.285 centimeter.
Annealed at 815°C for 10 minutes, water quenched.

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5. Seven reactor-grade zirconium rods 1.9 centimeters in diameter by 17.78 to 25.4 centimeters long and a large zirconium hexagon were hydrided to approximately N_H 6.2 (1.84 wt % hydrogen). The rods were all sound although the hexagon had one cracked face. Considering the size of the hexagon and that the hexagon and all the rods were additive-free, these results are encouraging. The hexagon is shown in Figure 4.1-7.

Fig. 4.1-7 - Reactor-grade zirconium hydrided to 1.84 weight percent hydrogen (N_H 6.2) using Brown Programmer with a cam cut for 15°F/hr (Neg. P63-6-4B)

Hydrided Titanium

The previous annual report described the work* that led to the successful development of massive titanium hydride material containing up to 3.9 weight percent hydrogen (N_H 8.9 to 9.0). This is the highest known hydrogen content of a massive solid material that is thermally stable at room temperature and above. Titanium hydride also has the following characteristics: (1) metallic in nature; (2) exhibits good dimensional stability and hydrogen retention in air at temperatures of 500°C and retains these characteristics after prolonged periods at temperatures up to 500°C; and (3) its physical properties enable it to be used as a self-supporting unclad structure for many applications. As identified in the previous annual report* the use of additives such as TiC, TiB₂, and B₄C permits the tailoring of physical and nuclear properties in accordance with the requirements of the mechanical - nuclear application. The present program continued the previous program of proof-testing, process improvement, and determination of additional physical property data.

*"Second Annual Report - High-Temperature Materials and Reactor Component Development Programs, Volume II - Materials," GE-NMPO, GEMP-177B, February 28, 1963, p. 234.

Fig. 4.1-8—Cross sections of cylindrical 13.6-kg titanium hydride specimen. This specimen was completely sound. Note the smooth cut face and the excellent uniformity of hydrogen concentration.

As previously reported,* several 13.6-kilogram slices from a 21-centimeter-diameter titanium ingot were hydrided in a single run. One of these pieces was sectioned to establish hydrogen concentration gradients. A photograph of the results showing hydrogen concentration values at 0.6-centimeter intervals is presented in Figure 4.1-8 and indicates that, over an area of approximately 5 by 12.7 centimeters, the average hydrogen concentration is 1.93 ± 0.02 percent.

Thermal Stability, Mechanical, and Physical Properties of TiH_x

Oxidation Resistance and Hydrogen Retention - To establish the oxidation resistance of this nominally 2 weight percent hydrogen titanium hydride, a 3- by 9- by 22-centimeter piece was cut from the cross section face next to that shown in Figure 4.1-8. This piece was sawed into blocks of approximately 2 by 2 by 3 centimeters. These blocks, together with seven zirconium hydride cylinders containing 1.96 weight percent hydrogen, were placed on test at 540°C in air. The specimen tray was rapidly removed into a room-temperature environment at 100- to 200-hour intervals to thermally shock the specimens and permit inspection. After the specimens were inspected, weighed and/or photographed, the specimen tray was rapidly reinserted into the test furnace. A photograph taken after a total of 1072 hours at 540°C is shown in Figure 4.1-9; no gross change in appearance can be noted. The specimen weight gain as a function of time was nominal. The data are plotted in Figure 4.1-10. The terminal curve shapes are indicative of a parabolic oxidation rate with little or no induction period.

Fig. 4.1-9 - Hydrided titanium and zirconium specimens after 1072 hours of testing at 540°C in natural convection air (Neg. P63-12-3)

* Ibid., pp. 237-238.

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Fig. 4.1-10—Average oxidation rates of hydrided titanium and zirconium specimens at 540°C

The average total weight gain for the hydrided titanium specimens after 1072 hours at 540°C was 0.075 percent, ranging from 0.056 to 0.105 percent, for the 24 specimens on test for the full interval. This compares with an average weight gain of 0.237 percent for the seven hydrided zirconium specimens and a range of 0.17 to 0.305 percent. Testing and evaluation of these samples will continue.

Modulus of Rupture - One of the purposes of the current series of investigations is to demonstrate that many hydrides, and particularly titanium hydride, are relatively ductile over a wide range of compositions and temperatures. Another objective is to demonstrate the long-life capability of these materials under typical operating conditions. As part of this study, representative specimens of the titanium hydride described above were removed from test after 456 hours or 1072 hours exposure and cut into bars measuring approximately 0.6 by 0.6 by 3 centimeters. Modulus-of-rupture tests (3-point suspension) were performed on these samples, and the test data are presented in Table 4.1-3. Although analysis of the hydrogen content of the specimen from the 1072-hour test has not been performed, the 456-hour test data show no hydrogen loss. Previous tests had shown nearly 100-percent hydrogen retention after extended testing at 540°C.* Therefore, the present tests indicate high strength and ductility of titanium hydride materials containing a nominal 2 weight percent hydrogen at temperatures above 350°C. Representative post-test samples of this material are shown in Figure 4.1-11.

Linear Thermal Expansion - The equipment used to conduct thermal expansion tests was reported previously.† The differential and total expansion data of a Ti - 5TiB₂ rod, hydrided to 3.13 weight percent hydrogen, ρ - 3.89 g/cm³, N_H 7.27, are plotted in Figure 4.1-12. The data show a room-temperature linear expansion of 5×10^{-6} cm/cm-°C and a 500°C linear expansion of 13×10^{-6} cm/cm-°C. The rod was 0.625 centimeter in diameter and 6 centimeters long.

*"High-Temperature Materials Program Progress Report No. 17, Part B," GE-NMPO, GEMP-17B, November 15, 1962, p. 14.

†"High-Temperature Materials Program Progress Report No. 31, Part B," GE-NMPO, GEMP-31B, January 24, 1964, p. 19.

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TABLE 4. 1-3

MODULUS OF RUPTURE^a OR MAXIMUM FIBER STRESS AT YIELD POINT OF TITANIUM HYDRIDE^{b, c, d, e}

Test Temperature, °C	Hours At 540°C	Cross Section Dimensions, mm		Load, kg	Modulus Of Rupture (Maximum Fiber Stress), kg/mm ²	Hydrogen Analysis After Test, wt%	Nature Of Fracture
		Height	Width				
20	456	6.53	8.02	199	24.8	1.93	Brittle
20	456	6.35	8.22	283	35.3	1.93	Brittle
20	456	6.22	7.90	358	44.6	1.92	Brittle
345	1072	8.25	6.02	658	34.4	-	Brittle
355	1072	6.26	6.90	406	49.9	-	Green stick-type fracture (Some evidence of ductility)
385	1072	7.15	5.96	621	65.0 ^f	-	None (ductile bend)
430	1072	8.10	6.20	544	47.5 ^f	-	None (ductile)
540	456	6.14	7.77	182	21.2 ^f	1.91	None (ductile)
540	456	8.12	5.98	250	21.6 ^f	1.91	None (ductile)
540	456	6.42	7.66	204	22.1 ^f	1.92	None (ductile)

^a3-point suspension (2.3 cm span)^bNominal hydrogen content 2 weight percent^cSpecimen cut from 13.6-kg ingot^dSpecimens tested after oxidation testing

$$eMR = \frac{MC}{I} = \frac{3}{2} \times \frac{Pl}{W(H)^2}$$

^fDuctile bend obtained in these samples - therefore, not a true modulus of rupture. Data shown for comparative purposes only.

*INDICATED MAXIMUM FIBER STRESS AT YIELD

Fig. 4.1-11 - Modulus-of-rupture specimens of hydrided titanium showing relative degrees of ductility from 343° to 427°C. Note slight deformation before breaking at 357°C (Neg. P63-12-7B)

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Fig. 4.1-12 - Linear thermal expansion of hydrided titanium

Calculations with these thermal expansion data permitted correction of the previously reported* tentative dynamic modulus data for this material.

The excellent ductility of titanium hydride containing approximately 2 weight percent hydrogen at temperatures above $350^\circ C$ indicates that this composition, which undergoes a phase change from $\alpha + \delta$ to $\beta + \delta$ to β , as the temperature is increased, may be capable of accommodating the associated volume changes and accompanying stresses by plastic flow.

The physical property and proof-test data completed during CY-63 demonstrated the excellent potential of high N_H titanium hydride as a high-temperature shielding material.

FUELED MODERATOR MATERIAL

Clad Fueled Yttrium Hydride

The objective of this study is the development of fueled hydride alloys of greater hydrogen stability at higher temperatures than the hydrided zirconium-base fuels. The useful operating temperature of such a system would be significantly above $760^\circ C$ and possibly as high as 950° to $1000^\circ C$ with presently available cladding. The development of such a fueled hydride would permit a significant advance in reactor design concepts. A literature search indicated that efforts of others to develop a hydrided yttrium - uranium fueled moderator were unsuccessful. Fusion metallurgy procedures were used and the immiscibility in the liquid state and the extreme differences in density of uranium metal and yttrium metal resulted in uncontrollable segregation of the uranium phase. The present study has resulted in the development of two basic processes for manufacturing hydrided yttrium containing uniformly dispersed uranium. One process employs hydrostatic pressing† and vacuum sintering while the other employs vacuum hot pressing. The former process offers the normal advantages of pressing and sintering, as compared with

* "High-Temperature Materials Program Progress Report No. 17, Part B," GE-NMPO, GEMP-17B, November 15, 1962, p. 15.

† "High-Temperature Materials Program Progress Report No. 29, Part B," GE-NMPO, GEMP-29B, December 6, 1963, p. 29.

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hot-pressing, e. g., multiple specimens per batch and better product uniformity. Accordingly, it has been used to prepare most of the specimens. Hydrostatic pressing of a mixture of hydrided yttrium and hydrided uranium powders followed by vacuum sintering for 1 hour at 1300°C results in a specimen of 97+ percent theoretical density with uniform uranium distribution and suitable for hydriding.

The vacuum hot-pressing procedure was also successfully employed. A blend of -325 mesh powders of hydrided yttrium and hydrided uranium was hot pressed at 1070°C for 1 hour at 10^{-3} mm Hg to produce homogeneous Y - 10U specimens of 97 percent of theoretical density. These specimens were then hydrided at 980°C to a hydrogen content of 1.89 percent. The microstructure of a typical specimen prepared by this method is shown in Figure 4.1-13.

Fig. 4.1-13 - Photomicrograph of Y-10U specimen made by vacuum hot pressing

Five hydrostatically pressed, sintered, and chromium-sprayed specimens of Y - 10U, hydrided to nominal N_H 5.1 and clad with 0.05-centimeter Fe-Cr-Al were tested in air at 950°C. As part of the evaluation program, two specimens were removed from test, one after 1000 hours and the other after 2000 hours, and examined chemically and metallographically. Chemical results showed no measurable change in hydrogen content. Figures 4.1-14 and 4.1-15 show the uniform bond between core and cladding of the specimen tested for 2000 hours.

The three remaining cylindrical Y - 10U specimens were nondestructively inspected after 3000 hours and 4000 hours of testing. A summary of the test data is presented in Table 4.1-4. The excellent condition of these samples after 4000 hours is illustrated in Figure 4.1-16. These samples are continuing on test at 950°C.

The excellent bench-test results of the hydrided yttrium - uranium after 4000 hours at 950°C in natural convection air indicate good performance should be realized during in-pile testing at the same temperatures. This prediction appears quite valid in view of previous studies which compared the bench-test and reactor results of unfueled hydrided yttrium and zirconium and the bench-test and reactor results of hydrided Zr-U.

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Fig. 4.1-14—Photomicrograph of core-cladding interface at hydried (nominal N_H 5), chromium-sprayed Y-10U specimen made by pressing and sintering technique, clad with 0.5 centimeter Fe-25Cr-5Al after 2000 hours at 950°C in air

Fig. 4.1-15—Cross section of the sample shown in Figure 4.1-13. Note the uniform bond between core and cladding around the entire periphery (Neg. P63-9-23)

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TABLE 4.1-4

WEIGHT AND DIMENSIONAL STABILITY OF Fe-Cr-Al-CLAD HYDRIDED Y - 10U SPECIMENS AFTER PROLONGED THERMAL STABILITY TESTING AT 950°C IN NATURAL CONVECTION AIR

Specimen Number	Before Testing		1000-Hr Data		2000-Hr Data		3000-Hr Data		4000-Hr Data		Hydrogen Content, %
	Weight, g	OD, cm	Weight, g	OD, cm	Weight, g	OD, cm	Weight, g	OD, cm	Weight, g	OD, cm	
11	90.1367	1.738	90.1484	1.737	-	-	-	-	-	-	1.63
12	78.3021	1.744	NT ^a	NT	-	-	-	-	-	-	1.56
13	90.1722	1.734	OT ^b	OT	90.1938	1.734	-	-	-	-	1.63
14	88.1215	1.731	OT	OT	OT	OT	88.1398	1.735	88.1385	1.738	OT
15	74.0464	1.730	OT	OT	OT	OT	74.0610	1.734	74.0586	1.737	OT
16	91.9702	1.745	OT	OT	OT	OT	91.9817	1.737	91.9808	1.743	OT

^aNT - Not taken, specimen was destroyed after autoclaving and used as a reference for as-fabricated hydrogen content.

^bOT - On test.

Fig. 4.1-16 - Hydrided Y-10U specimens clad with 0.05 centimeter Fe-Cr-Al after 4000 hours in natural convection air at 950°C (Neg. P63-12-8 A)

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Demonstration of the ultimate performance capability of hydrided Y - 10U is presently limited by the maximum cladding temperature. Earlier tests on hydrided Y-Cr showed much promise at 1200°C, but each test was terminated after 200 to 400 hours by cladding grain growth or interaction with the mounting structure. The maximum operating temperatures of both hydrided Y-Cr and hydrided Y-U should increase significantly, perhaps 200°C or more, if suitable compatible cladding alloys can be developed. Cladding materials capable of operation at still higher temperatures in air and/or liquid metals would permit an important advance in hydrided nuclear materials technology. Chromium- and molybdenum-base alloys have been identified which appear promising and will be investigated further for this purpose.

Fueled Zirconium Hydride

Canned zirconium hydride ($N_H \sim 6.0$) fuel elements are limited, for long-time service, to temperatures of 650°C to 800°C by the high equilibrium hydrogen pressures illustrated in Table 4.1-5. Because of the high hydrogen pressures, an essentially impervious hydrogen barrier is required to prevent loss of hydrogen at these high temperatures. The objective of this study is the development of improved hydrogen diffusion barrier materials that would provide containment of at least 95 percent of the initial hydrogen content over a reactor operating life of at least 10,000 hours. This barrier must be sufficiently ductile to accommodate flexure or swelling of the hydride fuel without cracking and loss of integrity. As indicated in Table 4.1-5, the hydrogen partial pressure of a Zr-U alloy hydrided to $N_H 6$ is approximately 1 atmosphere absolute at 800°C. This, then, is the pressure which the hydrogen barrier must successfully withstand throughout the life of a Zr-U hydride fuel element operating at 800°C.

TABLE 4.1-5
EQUILIBRIUM HYDROGEN PRESSURE
OF HYDRIDED ZIRCONIUM AS A FUNCTION OF
COMPOSITION AND TEMPERATURE

Hydrogen Content	Equilibrium Pressure, atmospheres			
	650°C	800°C	1000°C	1100°C
$N_H 6.6$	0.5	15	-	-
$N_H 6$	0.05	1	>40	-
$N_H 5$	<0.01	0.1	10	-
$N_H 4$	<0.01	0.1	10	-

As has been noted previously, carbon addition to zirconium improves the hydrided microstructure and performance characteristics.* However, each carbon atom effectively ties up a zirconium atom so that, if the hydrogen content per unit volume is held constant, the ratio of hydrogen atoms to the remaining zirconium atoms is increased, thereby increasing the hydrogen equilibrium partial pressures at high temperatures. Since the rate of pressure increase is nearly exponential with an increase in the hydrogen-to-zirconium ratio in this composition and temperature range, even a small carbon addition (0.01 to 0.1 wt %) causes a significant increase in pressure at temperature. Nevertheless, carbon additives have many advantages and are being employed in several advanced reactor concepts.

Evaluation of Pre-Oxidized Fe-Cr-Al as a Hydrogen Barrier in Non-Oxidizing Atmosphere - The results of the previously discussed work on Fe-Cr-Al-clad, hydrided yttrium demonstrated that a continuous aluminum oxide film on the cladding effectively limited

*Van Houten, op. cit.

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hydrogen loss. Since these results were obtained in an air atmosphere and any rupture in the oxide film would be healed by oxidation of the cladding, this work was directed primarily toward determining the effectiveness of aluminum oxide film on Fe-Cr-Al as a hydrogen barrier in non-oxidizing atmospheres.

An oxide film was provided by oxidizing (1 hour at 750°C in air) the surface of a Fe - 25Cr - 5Al alloy capsule prior to insertion of the Zr - 10U hydrided core. After the hydrided Zr - 10U (N_H 6.0) fuel elements are sealed within the oxidized Fe-Cr-Al cladding, they are tested in a flowing helium atmosphere at 750°C for long periods of time and then destructively analyzed for hydrogen content. Testing is performed on 40-gram fuel element specimens, and after test the entire specimen is consumed in several consecutive analyses. The average hydrogen content is then compared with the hydrogen content of the original as-hydrided bar. The precision of the hydrogen analysis is ± 0.01 percent absolute or 1 percent relative.

Two hydrided Zr - 10U specimens, clad only in oxidized Fe-Cr-Al, were held at 750°C for 1000 hours in the test apparatus. Analyses showed an average hydrogen loss of 1.05 percent of the initial hydrogen content. This would be equivalent to about a 10-percent loss in 10,000 hours if the rate of hydrogen loss is constant with time; a similar specimen tested for 2,000 hours at 750°C indicated a 1.02 percent hydrogen loss. Therefore, an initially high hydrogen loss rate apparently occurs during the early stages of testing at 750°C, followed by a much lower release rate. Further testing is necessary to define how long it would take Fe-Cr-Al-clad fuel elements to lose 5 percent of the original hydrogen at 750°C.

One of the potential uses of the hydrided Zr-U alloy would be as a homogeneous fuel and moderator element in a closed-cycle reactor where the fuel elements would be in contact with a liquid-metal heat-transfer fluid, such as a eutectic mixture of sodium and potassium. If the oxidized surface of the Fe-Cr-Al alloy is to serve as the principal hydrogen barrier, it must be protected from the corrosive effects of the liquid metal by a protective outer cladding such as Hastelloy N alloy. Two fueled specimens were clad with pre-oxidized Fe-Cr-Al with an outer cladding of Hastelloy N and tested at 750°C in a flowing helium atmosphere. Hydrogen analyses indicated that one specimen had lost 17 percent of its hydrogen during 1000 hours of testing and that the other had lost 19 percent in 1200 hours. These are excessive and unacceptable hydrogen loss rates. The results also indicate that the Al_2O_3 coating, formed by pre-oxidizing the Fe-Cr-Al, must retain its integrity if it is to remain effective as a hydrogen barrier.

Dual Purpose Claddings - A more direct approach to a hydrogen barrier material for hydrided Zr-U alloys used in liquid-metal cooled reactors would be a single cladding material which would serve a dual purpose as a hydrogen diffusion barrier and a metallurgically stable heat-transfer material to liquid-metal coolants. To investigate these possibilities, a series of experiments was initiated late in CY-63 employing Mo-Re and Cr-Ru as dual purpose barrier - cladding materials for hydrided Zr-U alloys. The high thermal neutron absorption cross section of Mo-Re would preclude its application as a fuel element cladding in thermal reactors but it is being used in this work as a reference hydrogen barrier material.

A Zr - 10U specimen hydrided to N_H 6.0 and clad with Mo - 50Re alloy completed a hydrogen retention test at 750°C for 1000 hours in a flowing helium atmosphere. Chemical analysis of the core material before and after testing indicated that 2.8 percent of the initial hydrogen content was lost during the test.

A second specimen clad with Cr-Ru alloy is presently on test at 750°C for the initial evaluation of this material as a hydrogen barrier for hydrided Zr-U alloy.

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Investigations of oxidized Fe-Cr-Al, Mo - 50Re, and Cr-Ru claddings will be continued to provide both quantitative and comparative data. Cladding will be tested on both hydrided Zr-U and hydrided Y-U, as well as on other hydride systems.

HIGH-TEMPERATURE CONTROL MATERIALS

The Eu_2O_3 -Ni cermet control rod with 80Ni - 20Cr cladding, developed under the GE-ANP program, has been tested at higher temperatures than any other known control rod assembly. The operating stability of this rod has been demonstrated in flowing air at 1000°C for periods of several thousand hours with repeated thermal cycling. Several of the newer reactor concepts, including those based on the Brayton cycle, could effectively exploit control rods with still higher temperature capabilities. Accordingly, the higher temperature control material work reported previously,* which indicated possible long-time stability of Eu_2O_3 at temperatures as high as 1650°C , offered promise in providing a suitable control rod material for these advanced applications. It was found that unclad Eu_2O_3 oxide, while relatively stable in argon, was not stable in dry hydrogen, but reduction of Eu_2O_3 in dry hydrogen at elevated temperatures could be almost totally inhibited by cladding the oxide in a refractory metal such as molybdenum. Since EuO and Eu_3O_4 , like Eu_2O_3 , are readily reduced in a dry hydrogen atmosphere at elevated temperatures, a study was made to determine if refractory-metal cladding would effectively inhibit the hydrogen reduction of EuO and Eu_3O_4 . These two oxides are potentially of greater interest than Eu_2O_3 , for some applications, because of their europium atom density (Table 4.1-6). There is also the possibility that the high-temperature stability of EuO and Eu_3O_4 is greater than that of Eu_2O_3 .

TABLE 4.1-6
EUROPIUM ATOM DENSITY OF
SEVERAL EUROPIUM OXIDES

Oxide	Density, g/cm ³	Atom Density, atoms Eu/cm ³
Eu_2O_3	7.28 ^a	2.48×10^{22}
	7.99 ^b	2.73×10^{22}
Eu_3O_4	8.11	2.82×10^{22}
EuO	8.21	2.94×10^{22}

^aLow-temperature form.

^bHigh-temperature form (monoclinic).

Powders of EuO and Eu_3O_4 were cold-pressed, sintered in argon at 1650°C , and enclosed in 0.05-centimeter Mo - 50Re cans with electron-beam-welded end caps. These specimens were then tested at 1650°C in a flowing dry (dewpoint, -54°C) hydrogen atmosphere.

After 500 hours at these conditions, both the EuO and Eu_3O_4 specimens appeared unchanged, showing no dimensional or weight changes. After 1000 hours, the cladding of the EuO specimen became distorted. With increasing time at temperature, the distortion was only slightly more pronounced, and its appearance after 1500 hours is shown in Figure 4.1-17. After 2000 hours of testing, neither specimen showed any significant weight change or leaks as analyzed by the mass spectrometer (helium) leak check.

*"Second Annual Report - High-Temperature Materials and Reactor Component Development Programs, Volume II - Materials," GE-NMPO, GEMP-177B, February 28, 1963, p. 249.

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Fig. 4.1-17—Mo—50Re-clad europium oxide specimens after 1500 hours at 1650°C in flowing dry (−54°C dewpoint) hydrogen (Neg. P63-5-27)

Metallographic examination revealed that there was no interaction between the Eu_3O_4 and the Mo - 50Re cladding. Figure 4.1-18 shows the EuO and Eu_3O_4 macrostructures, and Figures 4.1-19 and 4.1-20 show the microstructures after 2000 hours at test conditions of EuO and Eu_3O_4 , respectively. Grain growth in the Eu_3O_4 was relatively minor and there were no additional phases present in the microstructure. There were also no observed interactions between the EuO core and the Mo - 50Re cladding. However, the EuO apparently is not stable at 1650°C, because three distinct phases were found in the microstructure after 2000 hours of testing (Figure 4.1-19). It also exhibited excessive grain growth and dimensional distortion. Electron microprobe analysis indicated that the minor phase appearing as long needles was Eu_2O_3 and the trace phase within the needles was Eu_3O_4 . The manner in which the Eu_2O_3 and Eu_3O_4 were formed during the thermal exposure is not yet known. Further experimentation and analysis will be performed to explain the instability of EuO under these test conditions.

Crystallographic Studies of Europium Compounds

Previous crystallographic studies of europium-oxygen compounds revealed an unknown phase which was designated Ortho I because of the orthorhombic crystal structure.* Electron microprobe analysis of a single crystal of Ortho I showed the material to contain 7.1 percent silicon, which corresponds to an europium silicate of composition Eu_2SiO_4 , as originally suggested by Shafer.† This composition satisfies the observed unit cell and density values very well.‡

*"Second Annual Report—High-Temperature Materials and Reactor Component Development Programs, Volume II—Materials," GE-NMPO, GEMP-177B, February 28, 1963, p. 251.

†M. W. Shafer, IBM Research Center, Yorktown Heights, New York. Private communication.

‡"High-Temperature Materials Program Progress Report No. 25, Part B," GE-NMPO, GEMP-25B, July 31, 1963, pp. 30–31.

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Fig. 4.1-18—Sectioned specimens of EuO and Eu_3O_4 after 2000 hours at 1650°C in flowing dry hydrogen. Large void areas in the EuO were pulled out while sectioning the sample (Neg. P63-6-20)

Evaluation of Dysprosium and Gadolinium Oxides

The excellent thermal stability of Dy_2O_3 and Gd_2O_3 alone and in combination with refractory-metal powders as cermets, was discussed in a previous report.* Their physical and chemical stabilities are superior to the equivalent Eu_2O_3 bodies but their nuclear characteristics are somewhat inferior to those of europium for certain applications. Therefore, because of the superiority of Gd, Dy, and Eu, investigations of the several physical forms of each were continued. Small round rods of gadolinium, dysprosium, and samarium sesqui-oxides were fabricated by cold-extrusion and sintering to obtain modulus-of-rupture and linear-thermal-expansion test specimens. Details of the extrusion techniques were reported previously.† The Sm_2O_3 quickly hydrolyzed after sintering and tests could be performed only on Gd_2O_3 and Dy_2O_3 .

Modulus of Rupture - Extruded and sintered 0.635-centimeter diameter Gd_2O_3 and Dy_2O_3 rods were tested for modulus-of-rupture strength at room temperature and 1000°C in air. The average modulus-of-rupture value at room temperature for six Gd_2O_3 rods sintered to 93 to 99 percent of theoretical density was 902 kg/cm^2 ; the average value at 1000°C (five rods) was 633 kg/cm^2 . The average modulus-of-rupture value at room temperature for four Dy_2O_3 rods sintered to 98.7 percent of theoretical density was 484 kg/cm^2 ; the average value at 1000°C (five rods) was 388 kg/cm^2 .

Linear Thermal Expansion - Linear thermal expansion data for Gd_2O_3 and Dy_2O_3 were obtained using the direct observation method (micrometer telescope). Plots of this property as a function of temperature are shown for Gd_2O_3 in Figure 4.1-21 and for Dy_2O_3 in Figure 4.1-22. Also shown on the figures are Bureau of Mines‡ data obtained by high-temperature X-ray diffraction techniques using single crystals.

*"Second Annual Report—High-Temperature Materials and Reactor Component Development Programs, Volume II—Materials," GE-NMPO, GEMP-177B, February 28, 1963, p. 250.

†"High-Temperature Materials Program Progress Report No. 23, Part B," GE-NMPO, GEMP-23B, May 31, 1963, p. 31.

‡"Thermal Expansion and Phase Inversion of Rare Earth Oxide," Bureau of Mines, RI 5847, 1961.

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Neg. 3226

100 X

Fig. 4.1-19—Microstructure of EuO at the Mo-50Re interface after 2000 hours at 1650°C in hydrogen. The needlelike phase in the EuO matrix was not present prior to thermal exposure.

Neg. 3228

100X

Fig. 4.1-20—Microstructure of Eu_3O_4 in the core area showing grain size and voids after 2000 hours at 1650°C in hydrogen

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Fig. 4.1-21 - Linear thermal expansion of Gd_2O_3

SUMMARY AND CONCLUSIONS

The long-time nuclear and thermal stability of clad yttrium hydride was demonstrated over a 10,000- to 11,000-hour test period in natural convection air at 940° to 1050°C and in a reactor test at 880° to 940°C in air for 5000 hours. Another reactor test (LTYH_x-3) is still in progress after more than 6000 hours at this temperature.

Two approaches were developed for the production of clad hydrided Y-U fuel elements by powder metallurgy techniques. Thermal stability tests in air of this material clad with Fe-Cr-Al are still in progress after 4000 hours at 940°C. They show excellent hydrogen retention and dimensional stability characteristics. The powder metallurgy fabrication techniques should provide a very useful alternative to the fusion metallurgy techniques.

The technology for the hydriding procedures was extended. These extensions include the development of an automated cycle which significantly reduces direct labor costs and provides certain physical property improvements over some ranges of specimen size.

The titanium hydriding process was improved. Modulus-of-rupture, coefficient of thermal expansion, long-time oxidation stability through 540°C, and dynamic modulus evaluations of this material confirmed its suitability in nuclear applications. The material is capable of self-supported, unclad operation in air at temperatures up to 540°C. The use of additives such as TiC, TiB₂, B₄C, and WB₂ was shown to be acceptable; this indicates that performance can be tailored for maximum efficiency for shielding applications for mobile and SNAP system reactors, and other advanced applications.

The rare earth oxides of Eu, Gd, and Dy clad with Mo or Mo - 50Re have shown generally good thermal and dimensional stability after 2000 hours at 1650°C in dry hydrogen.

PLANS AND RECOMMENDATIONS

Fueled yttrium hydride materials have shown outstanding thermal stability, and development of these materials will continue, including cladding development for both gas-cooled and liquid-metal cooled applications, determination of mechanical properties, and in-pile tests.

Studies of the unfueled hydrides of titanium, zirconium, and yttrium will be continued, including determination of mechanical properties.

Studies related to air- and helium-cooled reactor control materials capable of 10,000-hour operation at 1200° to 1500°C will be continued.

4.2 DIRECT CONVERSION HIGH-TEMPERATURE MATERIALS RESEARCH (57011)

The objective of this work is to develop materials capable of high-performance operation in high-temperature, nuclear-powered, direct-conversion systems.

During CY-63, the scope of this program was three-fold:

1. Study and develop thermoelectric materials having a high figure of merit and capable of operating for long periods of time above 1000°C.
2. Develop and evaluate fabrication techniques for producing thermionic components required in long-life, high-efficiency, nuclear-fueled thermionic diodes.
3. Investigate and develop new refractory-metal thermocouple alloys and study the electrical resistivity of ceramics and the compatibility of high melting point ceramics with refractory metals.

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THERMOELECTRIC STUDIES

The objective of the present studies in high-temperature thermoelectric research is to develop materials having high dimensionless figures of merit over a wide range of temperature and to develop an understanding of the effects of metal additives on the thermoelectric properties of refractory oxides.

Y₂O₃-Stabilized ZrO₂ Cermets

The major portion of the high-temperature thermoelectric work performed during CY-63 was primarily concerned with the stabilized refractory oxide, ZrO₂, modified by the addition of metal to improve its thermoelectric properties.

In the investigation of ZrO₂ thermoelectric materials, both CaO and Y₂O₃ have been used for stabilization. Electrical conductivity of the stabilized material was found to be greatly enhanced by the addition of soluble metal. Zirconium was found to be the most suitable metal additive from measurements of electrical resistivity and Seebeck coefficient. Yttria-stabilized ZrO₂ specimens containing Zr metal were evaluated as a function of Y₂O₃ content ranging from 12 to 24 weight percent and Zr content ranging from 4 to 20 weight percent. The Seebeck coefficient and electrical resistivity determined in argon as functions of temperature for the compositions 24Y₂O₃ - 68ZrO₂ - 8Zr, 12Y₂O₃ - 80.2ZrO₂ - 7.8Zr, and 12Y₂O₃ - 79.5ZrO₂ - 8.5Zr are shown in Figures 4.2-1 and 4.2-2. These are typical of this series and show the effects of varying the composition of Y₂O₃ and Zr. The optimization parameter, S^2/ρ , for these materials is shown in Figure 4.2-3. The data indicated that the optimum Zr metal content for 12-percent Y₂O₃ material lies between 7.8 and 8.5 percent. The 24Y₂O₃ - 68ZrO₂ - 8Zr composition has a significantly higher electrical resistivity than the 12-percent Y₂O₃ material, indicating that greater benefit can be obtained by using less Y₂O₃ as a stabilizer. A curve determined from a sample of 12Y₂O₃ - 80ZrO₂ - 8Zr is included in Figure 4.2-3 for comparison.

CaO-Stabilized ZrO₂ Cermets

For comparison with the Y₂O₃-stabilized ZrO₂, CaO-stabilized ZrO₂ was also studied. The CaO-stabilized ZrO₂ was found to have thermoelectric properties similar to the Y₂O₃-stabilized material, with the advantages of lower sintering temperatures to form the desired microscopic dispersion of metal additives.

Metals other than Zr were added to CaO-stabilized ZrO₂ cermets. Samples were fabricated and tested containing Ti, V, Hf, and Y additives. Typical test results of some of the compositions, containing 8 to 10 weight percent metal additives, are shown in Figures 4.2-4 and 4.2-5. The compositions containing Ti and V typically have low Seebeck coefficients and high electric resistivities, indicating that these metals improve the thermoelectric properties of basic ZrO₂ but not as effectively as does Zr. The composition containing Y shows a reasonable Seebeck coefficient and a high electrical resistivity. The use of Hf as an additive resulted in gross deviations in the Seebeck coefficient depending upon whether the specimen was being heated or cooled. Further work is necessary before a comparison between Hf and Zr additives can be made.

Unstabilized ZrO₂ Cermets

During the course of experimentation it was noticed that metal additives appeared to strengthen the stabilized oxide composition. Accordingly, unstabilized samples of the composition 8Zr - 92ZrO₂ were prepared. The specimens had better thermoelectric properties than Y₂O₃-stabilized ZrO₂, and over a much broader temperature range. The linear expansion of stabilized and unstabilized ZrO₂ is shown in Figure 4.2-6. Although the unstabilized material experiences a large shift in linear expansion as it under-

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Fig. 4.2-1 - Seebeck coefficients of Y₂O₃-stabilized ZrO₂ compositions as a function of mean temperature

Fig. 4.2-2 - Arrhenius plot of Y₂O₃-stabilized ZrO₂ resistivities

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Fig. 4.2-3 - Optimization parameters, S^2/ρ , of Y_2O_3 -stabilized ZrO_2 compositions

goes the monoclinic-to-tetragonal phase change, the specimen maintained its physical integrity upon cooling and did not shatter.

Other tests showed that this composition also has better thermal shock resistance than either stabilized ZrO_2 or stabilized ZrO_2 containing Zr additive. These tests consisted of water quenching of heated specimens and heat shocking with an electron beam.

Additional specimens of Zr- ZrO_2 compositions were fabricated containing from 6 to 9 weight percent Zr. As expected, both the Seebeck coefficient and the electrical resistivity increased with decreasing metal content. The variation in electrical resistivity of Zr- ZrO_2 as a function of metal content and temperature was reported previously.* Distinct breaks in the heating and cooling plots of electrical resistivity occurred in the tem-

*"High-Temperature Materials Program Progress Report No. 27, Part B," GE-NMPO, GEMP-27B, September 30, 1963, pp. 60-63.

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Fig. 4.2-4 - Seebeck coefficients of stabilized ZrO_2 compositions containing Ti, V, and Y metal additives

Fig. 4.2-5 - Arrhenius plot of the electrical resistivities of stabilized ZrO_2 compositions containing Ti, V, and Y metal additives

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Fig. 4.2-6—Linear thermal expansion of stabilized $12\text{Y}_2\text{O}_3 - 79.8\text{ZrO}_2 - 8\text{Zr}$ and unstabilized $8\text{Zr} - 92\text{ZrO}_3$

perature range from 1500° to 1600°C . The optimization parameter, S^2/ρ , for several of these compositions is shown in Figure 4.2-7. The S^2/ρ values for the best previously developed material, $12\text{Y}_2\text{O}_3 - 80\text{ZrO}_2 - 8\text{Zr}$, are included for comparison. In the temperature range from 1500° to 1950°C there is a decided improvement in the S^2/ρ values over the earlier material. Of the compositions tested, $7\text{Zr} - 93\text{ZrO}_2$ results in the highest average S^2/ρ value. Since the Seebeck coefficients were measured with a temperature difference of 150°C , the $7\text{Zr} - 93\text{ZrO}_2$ material is usable to good advantage over a temperature gradient of 700° to 800°C . Assuming that the thermal conductivity of these new materials is approximately the same as that previously measured for $12\text{Y}_2\text{O}_3 - 80\text{ZrO}_2 - 8\text{Zr}$ * the average dimensionless figure of merit ($ZT = S^2T/\rho k$) for $7\text{Zr} - 93\text{ZrO}_2$ in the temperature range from 1575° to 2275°C is about 0.38. This corresponds to a maximum conversion efficiency of about 2.5 percent. Because of this low conversion efficiency, the material is best suited where a high heat rejection temperature is desirable.

Y_2O_3 Cermets

In the course of this work, compositions of Y_2O_3 containing 5, 6, 7, and 10 percent Y additives were fabricated and tested. The Seebeck coefficients and electrical resistivities

* "Second Annual Report—High-Temperature Materials and Reactor Component Development Programs, Volume II—Materials," GE-NMPO, GEMP-177B, February 28, 1963, p. 257.

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Fig. 4.2-7 - Optimization parameters (S^2/ρ) of Zr-ZrO $_2$ compositions

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of these compositions were reported previously.*† The Seebeck coefficients and electrical resistivities of the samples containing 7 and 10 percent Y additives are similar and indicate that these samples are too metallic in thermoelectric properties. The specimen containing 5 percent Y has a sizeable negative Seebeck coefficient with respect to tungsten over an extensive temperature range. Although the electrical resistivity is somewhat higher than desirable, a slight adjustment in composition may produce an attractive energy conversion material.

U-UO₂ Cermets

A powder metallurgy specimen of U-UO₂ was fabricated using -325 mesh UO₂ and hydrided U. The materials were blended and isostatically pressed, followed by sintering in argon at 2000°C. The first composition studied was 11.2U - 88.8UO₂. The thermoelectric properties of UO₂ reported previously‡§ showed a polarity reversal in the Seebeck coefficient at approximately 1350°C. The present studies indicate that the addition of U reduces the temperature of the Seebeck polarity reversal to about 500°C. Similar to the earlier findings with metal additions to ZrO₂ and Y₂O₃, the U-UO₂ composition is n-type at high temperatures. The Seebeck coefficient of U-UO₂ and an Arrhenius plot of the electrical resistivity of the 11.2U - 88.8UO₂ system were reported previously.¶ The optimization parameter S^2/ρ values are shown in Figure 4.2-8. These results are quite encouraging in comparison to those found for the ZrO₂-base material.

Device Fabrication

A simple power-producing device was assembled and tested using the Zr-ZrO₂ thermoelectric material. A specimen of 7Zr - 93ZrO₂ material was fabricated in the shape of a rod, about 7.5 centimeters long and 1 centimeter in diameter, with conical ends. The conical ends were mated to matching holes in molybdenum pieces to form the hot and cold junction electrical contacts. The natural temperature gradient of a small high-temperature furnace was used to operate the device at hot and cold junction temperatures of 2200°C and 1900°C, respectively. A short circuit output current of about 1.5 amperes was obtained for the duration of the 2-hour test. The open circuit voltage obtained was 80 millivolts. The short circuit current and the voltage measured agree with that calculated from the Seebeck coefficient and electrical resistivity of the material. Further work in the direction of evaluations of these materials under power-producing conditions is underway.

THERMIONIC MATERIALS RESEARCH

Refractory metals with UO₂ as a nuclear fuel were investigated to establish the useful upper temperature limitations of these materials in high-performance thermionic energy conversion. Work on high-temperature refractory-metal-clad nuclear fuel elements under Job 57005, "Refractory-Metal Fuel Element Materials Research," has indicated encouraging stability at high-temperature between UO₂ and the refractory metals.

Preparation of Thermionic Test Specimens

Uranium dioxide - refractory-metal test specimens were initially prepared by simply canning UO₂ - refractory-metal cores in a suitable refractory-metal container. Early

* "High-Temperature Materials Program Progress Report No. 25, Part B," GE-NMPO, GEMP-25B, July 31, 1963, pp. 52-53.

† "High-Temperature Materials Program Progress Report No. 29, Part B," GE-NMPO, GEMP-29B, December 6, 1963, p. 73.

‡ "First Annual Report - High-Temperature Materials and Reactor Component Development Programs, Volume II - Materials," GE-NMPO, GEMP-106B, February 28, 1962, p. 173.

§ "Second Annual Report - High-Temperature Materials and Reactor Component Development Programs, Volume II - Materials," GE-NMPO, GEMP-177B, February 28, 1963, p. 271.

¶ "High-Temperature Materials Program Progress Report No. 31, Part B," GE-NMPO, GEMP-31B, January 24, 1964, pp. 42-43.

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Fig. 4.2-8—Optimization parameter (S^2/ρ) of 11.2U—88.8UO₂

experiments showed that specimens made in this manner developed blisters when thermocycled. It was found that the blisters could be eliminated by gas pressure bonding the specimen, forming a metallurgical bond at the cladding - core interface. This method was used to produce bonded seals between cladding interfaces of Ni, Ta, Mo, and W.

Typical examples of the thermionic emitter configurations closed by diffusion bonding are shown in Figure 4.2-9. Figure 4.2-9a is a button-type emitter used for evaluating uranium diffusion through the refractory-metal cladding at various temperatures. Figure 4.2-9b shows the geometry of the LASL-type emitter specimen consisting of an enriched fuel core of W - 60UO₂ clad with Nb.

Diffusion Rates of Refractory Metals

To establish temperature- and time-dependence of various metal combinations, a series of diffusion studies was conducted on various refractory metals and alloys joined by gas pressure bonding using 700 kg/cm² gas pressure at 1650°C for 1 hour. The first study consisted of the examination of bonded interfaces between W, W - 26Re, Mo, Mo - 50Re, and Nb by metallographic techniques followed by electron-microprobe analysis of the bonded materials to determine the extent of interdiffusion of the components

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a. Nb-CLAD ENRICHED W - 60UO₂ (VOL %)
THERMIONIC EMITTER

b. FUELED BUTTON-TYPE EMITTER
CLAD WITH MOLYBDENUM

Fig. 4.2-9 - Typical fueled thermionic emitters prepared by gas pressure diffusion bonding

during bonding. Photomicrographs and associated microprobe traces of the specimens in this study were published previously.* Examination of the data reveals some interesting diffusion information concerning the rates of diffusion of some materials in relationship to others. The widths of the diffusion zones varied from 5 to 36 microns with the junctions containing Nb having the most extensive diffusion. Very slight interdiffusion was noted between W and either Mo or W - 26Re.

HIGH-TEMPERATURE METAL - CERAMIC VACUUM SEAL

Reliable, long-time operation of a thermionic conversion device will require an electrically insulated power lead through the diode capsule wall. This insulated lead, involving a metal - ceramic seal, must be capable of maintaining the capsule's operating environment. A seal which operates at or near the diode's collector temperature will simplify the design by making it unnecessary to place the seal away from the collector in an area of lower temperature.

An investigation into the possibility of fabricating seals by use of a high-temperature, high-pressure process was initiated. A comparison of the thermal expansion data of re-

*"High-Temperature Materials Program Progress Report No. 31, Part B," GE-NMPO, GEMP-31B, January 24, 1963, pp. 46-55.

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fractory metals and ceramics revealed that Nb and Al_2O_3 or Y_2O_3 had similar properties making them favorable for the development of a metal-to-ceramic seal that could undergo heating and cooling without developing high-stress areas at the interface.

Attempts to join Nb to various ceramics under 700 kg/cm^2 gas pressure at 1650°C resulted in visibly bonded interfaces. The initial bonding attempts with a coaxial tube geometry resulted in radial cracking of the ceramic member. Additional work produced several metal - ceramic assemblies that appeared to be well bonded with no evidence of radial cracking of the ceramic member.

In one series of experiments, Lucalox* Al_2O_3 tubes were vacuum encapsulated in Nb cans with various inner and outer wall thicknesses. After bonding, the specimens were sectioned and examined metallographically. Good visual bonding was obtained on all specimens, but radial cracking of the ceramic material occurred unless the inner metallic tube wall was thin with respect to the ceramic wall thickness. Figure 4.2-10 is a photomicro-

Fig. 4.2-10— Photomicrographs showing the interface of Lucalox (Al_2O_3) bonded to niobium using 700 kg/cm^2 gas pressure at 1650°C for 1 hour

*Trademark of the General Electric Company for commercial polycrystalline alumina.

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graph of a crack-free, bonded specimen having 0.81-millimeter inner and outer metal wall thicknesses and a ceramic outside diameter of 2.22 centimeters with a 6.4-millimeter wall thickness. Similar results were obtained with assemblies consisting of Lucalox tubing of 1.59 centimeters outside diameter and 1.27 centimeters inside diameter clad inside and out with 0.25 millimeter Nb.

A second series of experiments was made to determine the possibility of using flame-sprayed ceramic coatings as a means of obtaining a thin seal. A 0.25-millimeter ceramic coating of Al_2O_3 and Y_2O_3 was flame sprayed on two 1.2-centimeter-diameter solid Nb mandrels. The mandrels were then vacuum encapsulated in Nb and high-temperature pressure bonded. Examination disclosed radial cracking in the Al_2O_3 assembly, but the Y_2O_3 assembly was without cracks and visually bonded. Metallographic examination indicated an excellent mechanical bond.

A similar flame-sprayed Y_2O_3 specimen, which was thermal cycled rapidly from 100° to 1600°C five times in an argon atmosphere with a total time at temperature of 1.5 hours, is shown in Figure 4.2-11 with the interfaces shown on the inset. The unevenness of the metal-to-ceramic interface is characteristic of flame-sprayed oxide deposits. No degradation of the interface was apparent as a result of the thermal cycle treatment.

Further evaluation will be performed on this type of seal to determine if the environmental condition required of thermionic devices at high temperatures can be maintained for long periods of time.

HIGH-TEMPERATURE THERMOCOUPLE DEVELOPMENT

The ever increasing need for monitoring and controlling extremely high temperatures for long periods of time makes it necessary to develop reliable instrumentation. In support of the testing work on Ta-clad W- UO_2 fuel elements being performed under Job 57005 and the high-temperature testing of thermoelectric and thermionic components under this job, a portion of the overall direct conversion effort is being applied toward the development and evaluation of high-temperature thermocouples.

High-temperature thermocouple work during CY-63 consisted of electrical resistivity measurements of insulators, comparison of BeO and ThO_2 insulation on W / W - 26Re thermocouple electrical output, and thermocouple alloy development.

Electrical Resistivity Measurements of Insulators

In the course of investigating the performance of high-temperature refractory-metal thermocouples, it was found that degradation in performance can usually be traced to the ceramic materials which insulate the thermocouple in the vicinity of the hot junction. At high temperatures, the electrical resistivity of the commonly used ceramics becomes comparable to the resistance of the thermocouple and develops a shunt path for the thermoelectric signal. This results in an erroneously low output from the thermocouple. Accordingly, part of the present investigation is the determination of the high-temperature electrical resistivity of potential ceramic insulators.

The electrical resistivities of holmium oxide (Ho_2O_3), lutetium oxide (Lu_2O_3), ytterbium oxide (Yb_2O_3), hafnium oxide (HfO_2), and thulium oxide (Tm_2O_3) were evaluated to approximately 2000°C . The electrical resistivity results and the methods used in this evaluation were reported previously.* At temperatures below about 1760°C , HfO_2 showed the highest resistivity. The HfO_2 phase change was shown to occur in the temperature range 1760° to 1800°C . A possible phase change was observed to occur in Ho_2O_3 in the temperature range 1540° to 1725°C upon heating and at about 1540°C upon cooling. Above

* "High-Temperature Materials Program Progress Report No. 25, Part B," GE-NMPO, GEMP-25B, July 31, 1963, pp. 57-59.

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Fig. 4.2-11 – Photomicrographs showing the flame sprayed Y_2O_3 and niobium interfaces after five rapid thermocycles ranging from 100° to $1600^\circ C$

$1770^\circ C$, Tm_2O_3 showed the highest electrical resistivity with a value of about 35 ohm-centimeters at $2000^\circ C$. Of the materials tested, Yb_2O_3 had the lowest electrical resistivity with a value of about 7 ohm-centimeters at $2000^\circ C$.

BeO and ThO_2 Insulation on W / W - 26Re Thermocouples

A comparison was made of the effectiveness of BeO and ThO_2 insulators in W / W - 26Re thermocouples. The comparative technique used in these tests was based on the fact that the thermoelectric signal of the W / W - 26Re thermocouple increases almost linearly with temperature to as high as $3200^\circ C$. Consequently, any abnormalities developing dur-

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ing the temperature rise causing gross deviation from the known thermoelectric output may be attributed to electrical shorting through the insulation material. The insulated thermocouples were located at the center of the hot zone of a tantalum heating element of a high-temperature electrical resistance furnace.

The test results on ThO_2 and BeO insulators are shown in Figure 4.2-12. The curves show that below 2200°C the ThO_2 - and BeO -insulated thermocouples performed equally well and both were satisfactory. At 2250°C , the ThO_2 -insulated thermocouple began to deviate from the standard curve. The BeO -insulated thermocouple performed well to approximately 2430°C , or within 30° of its melting point, before an anomaly in its output occurred. On the basis of these tests, the use of ThO_2 should be limited to 2250°C and the use of BeO to approximately 2400°C . No evidence was found of reaction occurring between the 0.5-millimeter W / W - 26Re thermocouple wires and either the BeO or ThO_2 insulators after 1 hour at 2430°C and 2250°C , respectively.

Fig. 4.2-12 - Comparison of BeO and ThO_2 insulators on W / W - 26Re thermocouples showing deviation in electrical output signal

High-Temperature Thermocouple Alloy Development

Osmium - Osmium has a melting point of 3000°C , which is exceeded only by W and Re. An Os rod was fabricated, as reported previously,* and its thermoelectric properties were measured to temperatures above 2000°C .

Figure 4.2-13 compares the thermoelectric output of Os with other refractory metals referenced to W - 26Re. This comparison shows that Os is more thermoelectrically negative than the other refractory metals. The use of Os with W or Mo offers a system having a greater sensitivity than the conventional W / W - 26Re thermocouple.

Tc and W-Tc Thermoelement Materials - An investigation on Tc was conducted to establish its thermoelectric properties. Technetium is known to be chemically and metallurgically similar to Re and from the nuclear standpoint has the advantage of a lower neutron absorption cross section. The Tc powder, -100 mesh, was isostatically pressed at 20,000 psi into 43-centimeter-long rods.

*"High-Temperature Materials Program Progress Report No. 27, Part B," GE-NMPO, GEMP-27B, September 30, 1963, p. 69.

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Fig. 4.2-13—Thermoelectric output of the refractory metals with respect to commercial W-26Re as a function of temperature

The thermoelectric output characteristic of Tc is shown in Figure 4.2-13. Comparing the curves of Tc and Re, it is surprising to find such close agreement between the two elements even though both are similar in many respects. A melting point of approximately 2200°C limits the usefulness of Tc as a very high-temperature thermocouple material, but by alloying it with other metals, its upper temperature range can be extended. It was alloyed with W and produced a material capable of measuring temperature to at least 2500°C.

The W - 5Tc (at. %) was prepared in a similar manner to Tc except that the powders of W and Tc were -325 mesh and the Tc had been chemically purified before blending. The

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W - 5Tc alloy was evaluated for its thermoelectric output with respect to W - 26Re commercial wire. Figure 4.2-13 shows the thermoelectric output to be higher than that found for pure W or W - 5Re (W - 4.94 at. % Re). The W - 5Re thermoelectric output relative to tungsten decreases with increasing temperature until it is equal to the output of W at approximately 1900°C. On the other hand, the W - 5Tc thermoelectric output is higher than W to the highest temperature measured (approximately 2400°C). The W - 5Tc thermoelectric output characteristic is definitely superior to W or W - 5Re. Additional W-Tc alloys were prepared and are being evaluated to determine the most thermoelectrically positive alloy in this system.

Co-Re Alloys - Laboratory experience has shown that Pt / Pt - 10Rh, and chromel / alumel thermocouples lose calibration in the absence of oxygen. Accurate temperature measurement in high-temperature oxygen-free environments can be a serious problem. Further developments in thermocouple technology are necessary to permit accurate temperature measurements in inert and reducing environments at intermediate and high temperatures.

A series of investigations was undertaken to evaluate the thermoelectric properties of Ru and Os alloys. Cobalt was selected for initial evaluation because it is structurally similar to Os, Re, and Ru, all having a close-packed hexagonal crystal structure. Cobalt-rhenium alloys are also known to form a continuous series of solid solutions.* The melting points of the Co-Re alloys are lower than refractory-metal alloy systems and consequently would restrict their use to the intermediate-temperature region. Such a system, however, can still be very useful if an alloy composition could be found that exhibits improved thermoelectric properties over the existing thermocouple materials. A series of Co-Re alloy specimens was prepared. Metallographic examination showed all specimens to be single phase.

The thermoelectric output of the alloys in contact with 0.5-millimeter W - 26Re wire was measured as a function of temperature in a hydrogen environment using a calibrated W / W - 26Re thermocouple to monitor the junction temperature.

The measured thermoelectric outputs for the Co-Re alloys are shown in Figure 4.2-14. The thermoelectric signal generated from a thermocouple formed from any two of the alloys can be determined by taking the difference between the curves. It is interesting to note that normally negative Re becomes positive when alloyed with a small addition of normally negative Co. Of significance in the further development of alloys, a Co-Re composition containing approximately 10 weight percent Co results in the most thermoelectrically positive material when measured with respect to W - 26Re. The addition of Co to Re in excess of 20 weight percent Co results in a steady decrease in the positive thermoelectric output, taking a sharp drop in the negative direction with Re alloys containing over 75 percent Co. Comparing the data presented in Figure 4.2-14 with handbook values for Pt / Pt - 10Rh and chromel / alumel thermocouples, it is evident that a thermocouple consisting of Co / Re - 10Co will generate a thermoelectric signal at 1000°C equivalent to chromel / alumel and greater by a factor of four than that generated by a Pt / Pt - 10Rh thermocouple.

From the economic standpoint, it would be better to use alloys in the Co-Re system with large percentages of Co to reduce the amount of expensive Re necessary. From the curves shown in Figure 4.2-14, it can be seen that the Re - 75Co alloy could be used versus Co and yet obtain a good electrical response.

Re-Ni Alloy - Cobalt and nickel are highly thermoelectrically negative materials with respect to W - 26Re. Because of this similarity, the Re-Ni system was also investigated.

*M. Hansen, *Constitution of Binary Alloys*, Second Edition, McGraw-Hill Book Co., Inc., New York City, 1958, pp. 494-495.

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Fig. 4.2-14 - Measured thermoelectric output of Co and Co-Re alloys in hydrogen as a function of temperature

Figure 4.2-15 shows the comparison between the thermoelectric outputs of Re - 5Ni, Re - 10Ni, Re - 20Ni, Re - 95Ni, and Ni. The curves are generally similar to the Co-Re curves of Figure 4.2-14. In both cases, small additions of Re altered the highly thermoelectrically negative material to a thermoelectrically positive material.

In summary, the experimental work with Re additions to thermoelectrically negative material has resulted in alloys becoming more positive than either of the parent metals. Rhenium additions to Os appear to cause a similar trend. This work has identified a

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Fig. 4.2-15—Measured thermoelectric output of Ni and Re-Ni alloys in hydrogen as a function of temperature

number of interesting possibilities; foremost is the possibility of either a Ni-Re or Co-Re thermoelement system which may have potential for temperature measurement to 1400°C, giving a signal comparable to that of the chromel / alumel thermocouple, but a signal that does not drift when operated in oxygen-free atmospheres.

Refractory-Metal Thermocouple Wires

Thermocouple calibration work in the past has strongly indicated a lack of uniformity of refractory-metal thermocouple wire. To establish the extent that the wire varies from

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lot to lot, a series of measurements was undertaken to evaluate the deviations in the thermoelectric output of various wire lots.

Six samples each of W and W - 3Re and four samples of W - 20Re thermocouple wires, all approximately 0.25 millimeter in outside diameter, were evaluated. They were manufactured by standard techniques that should have insured homogeneity of microstructure and uniform chemical composition throughout each lot. A photograph and description of the apparatus used in these tests were reported previously.*

The first series of tests consisted of uniformity checks on six samples of pure W wire. Initially, three W ingots were prepared by powder metallurgy techniques. Two samples of wire were drawn from two different sections of each ingot. The thermoelectric output of each W wire as a function of temperature was measured with respect to a reference W wire designated as wire No. 6. The results of the evaluation showing the difference found in each wire are shown in Figure 4.2-16. The largest deviation, amounting to 18°C , was found to exist between the reference wire (No. 6) and wire No. 2 at 2000°C . If the wires had been chemically or structurally identical, no thermoelectric signal would have been generated.

Using identical procedures, six W - 3Re thermocouple wires were drawn and evaluated against a reference W - 3Re thermocouple wire. The results of the evaluation with wire No. 12 designated the reference wire are shown in Figure 4.2-17. The spread in data covers approximately -80 microvolts which is approximately 5°C . The small Re addition apparently improved the uniformity of thermoelectric output over that of pure W.

In another test, four W - 3Re wires, each 1 meter long, were used to determine the variation of thermoelectric output in a single wire. The section designated "a" in Figure 4.2-18 was selected as a reference, for comparing the thermoelectric uniformity of the other sections. As can be seen, the greatest deviation amounted to approximately 20 microvolts (1°C) between the a and d section. This slight deviation indicates that the drawn wire was very uniform throughout its length.

The last evaluation series was four W - 20Re thermocouple wires, drawn in a similar manner as the wires in the other evaluations. The results of the evaluation with wire No. 14 designated the reference wire are shown in Figure 4.2-19. As can be seen, the greatest thermoelectric output variation is approximately -20 microvolts (1°C), indicating that the wires were uniform both in chemical and structural makeup.

In applications where W / W - Re thermocouples are used to measure the temperature differences, the above data indicate that significant errors may be possible, due to thermoelectric variations in the tungsten leg. Future thermocouples of W - 3Re alloys versus other W - 26Re alloys would probably be more reliable than W / W - 26Re alloy thermocouples.

SUMMARY AND CONCLUSIONS

Seebeck coefficients and electrical resistivities of various ZrO_2 , Y_2O_3 , and UO_2 base compositions were measured. One simple power-producing device, tested to 2000°C using $7\text{Zr} - 93\text{ZrO}_2$ as a thermoelectric material, showed that the short-circuit current and open-circuit voltage agreed with that calculated from the Seebeck coefficients and electrical resistivities of the materials.

Work on refractory-metal-clad W- UO_2 core thermionic emitters showed that gas pressure bonding at 1650°C under 700 kg/cm^2 pressure can be used to prepare specimens of complicated configuration and to close tolerances. Studies were initiated to establish the rates of interdiffusion of refractory metals as a function of time and temperature.

* "High-Temperature Materials Program Progress Report No. 29, Part B," GE-NMPO, GEMP-29B, December 6, 1963, pp. 84-85.

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Fig. 4.2-16— Thermoelectric output as a function of temperature of six commercial tungsten wires with respect to wire No. 6

Fig. 4.2-17— Thermoelectric output as a function of temperature of six commercial W-3Re (wt %) wires with respect to wire No. 12

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Fig. 4.2-18—Thermoelectric output as a function of temperature of one W-3Re (wt %) wire with respect to wire No. a

Fig. 4.2-19—Thermoelectric output as a function of temperature of four commercial W-20Re (wt %) wires with respect to wire No. 14

High-temperature metal - ceramic seals were fabricated by gas pressure bonding techniques. Interface bonds between the metal and ceramic are sufficiently strong to take numerous thermocycles without cracking.

Development of high-temperature thermocouples were concerned mainly with insulators and alloy development of thermoelements. The electrical resistivities of Ho_2O_3 , HfO_2 , Tm_2O_3 , Lu_2O_3 , and Yb_2O_3 were measured to 2000°C . BeO and ThO_2 should not be used above 2400°C and 2200°C , respectively, as insulators on W / W - 26Re thermocouples. The thermoelectric properties of pure Os, Tc, Co, and Ni were determined. Alloys of W-Tc, W-Re, Co-Re, and Ni-Re are promising as thermocouple materials. In the W / W - Re system, tungsten was less uniform in emf than W-Re alloys.

PLANS AND RECOMMENDATIONS

Work on the fabrication and testing of simple thermoelectric devices using ZrO_2 cermetts will be emphasized. In addition, studies of new experimental cermetts for use as thermoelectric materials will be conducted.

Fabrication and testing of thermionic emitters to study the compatibility of UO_2 fuel with refractory metals will be continued. Development and testing of high-temperature metal-to-ceramic seals by gas pressure bonding will be studied. The rates of interdiffusion of refractory metals and their alloys as a function of time and temperature will be determined.

Further studies will be conducted on various refractory-metal systems in an effort to develop thermocouples of longer life with higher emf outputs. Studies will be carried out on the high-temperature compatibility of various refractory oxides with refractory-metal systems.

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4.3 HIGH-FLUX REACTOR MATERIALS GASEOUS FUELS RESEARCH (57074)

The objective of this program is to investigate pertinent materials problems which would arise in the design and construction of reactors in which the fissioning material is embodied in a gas at high temperature (5000°K minimum).

CORROSION INVESTIGATIONS

Corrosion studies planned under this task include exposing certain potential container materials such as Al_2O_3 , SiO_2 , MgO , and BeO to the hot vapors of various uranium halides. Because of its high volatility and ready availability, UF_6 is of particular interest.

An apparatus was designed for exposing Al_2O_3 specimens to UF_6 gas at a temperature of approximately 1000°C after a pretreatment with F_2 to condition the surfaces exposed to UF_6 . While safeguards for the handling of F_2 are being prepared, corrosion tests with other uranium halides have been started in the apparatus which is shown in Figure 4.3-1. UCl_3 was synthesized in the apparatus using the reactions:

The product was identified as UCl_3 by X-ray diffraction. Commercially available anhydrous uranium halides will also be used in these tests.

Fig. 4.3-1 - Schematic of apparatus used to investigate the effects of uranium halide vapors on refractory oxides

THERMODYNAMIC STUDIES

A computer program for calculation of selected thermodynamic functions of gases was written and is being checked. If the necessary molecular and spectroscopic data are available, the program will compute the following quantities for atoms, ions, and linear or nonlinear molecules:

Free energy function:

$$- \frac{F^0 - H^0_{T_{\text{ref}}}}{T}$$

Enthalpy function:

$$\frac{H^0 - H^0_{T_{\text{ref}}}}{T}$$

Entropy:

$$S^0 - S^0_{T_{\text{ref}}}$$

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As presently written, the program assumes that the gases are at a pressure of 1 atmosphere, that they obey the perfect gas law, and that the molecules behave as harmonic oscillators and rigid rotators. When satisfactory agreement with published data is obtained, more exact approximations will be investigated.

THERMAL AND NUCLEAR STUDIES

Thermal and nuclear data are needed to guide the choice of materials to be studied and the conditions under which they will be tested. The type of information needed for each assumed reactor type includes a delineation of the useful gaseous fuel temperature levels, the associated thermal and nuclear radiation intensities, a description of the thermal profiles to be anticipated, and an estimate of the heat loads and maximum wall temperatures to be expected.

The initial work dealt with gaseous core reactor (GCR) rocket propulsion systems. The nuclear fuel temperature requirements were evaluated first* as a function of thrust level and unshielded engine thrust-to-weight ratio for graphite-reflected reactors of a particular geometry. This work was then extended to include gamma-shadow-shielded engine thrust-to-weight ratio.† At that time, the variables were divided into two groupings: (1) engine thrust-to-weight ratio, thrust level, and active core diameter, and (2) specific impulse, net thrust, radiation heat transfer area, and solid component heating fraction.

During this reporting period, the variation of hydrogen specific impulse with temperature as a function of nozzle pressure ratio was determined, the limits imposed on attainable specific impulse by ultraviolet transparency of container materials and solid component heating were delineated, the effect of nuclear fuel pressure level on attainable engine thrust-to-weight ratio was calculated, and an analytical model for evaluation of container-material heating by thermal conduction from the nuclear fuel was studied.

Hydrogen Specific Impulse Temperature Requirements

As was noted in a previous report,‡ useful nuclear fuel temperatures are a function of the specific impulse, reactor radiation heat transfer area geometry, engine thrust-to-weight ratio, and engine thrust level. This discussion presents hydrogen specific impulse as a function of propellant temperature. The nuclear fuel temperature must exceed the propellant temperature to a degree dependent on the other parameters mentioned above.

Figure 4.3-2 presents the variation in hydrogen specific impulse with pre-expansion total temperature, T_c , for nozzle pressure ratios of 100 and 1000 for frozen isentropic and isothermal expansion processes. Equilibrium isentropic expansion is presented for a nozzle pressure ratio of 1000 only. The pre-expansion total pressure was assumed to be 100 atmospheres.

Specific impulses for frozen isentropic expansion have been determined utilizing an unpublished computer code.§ This code computes specific impulse, including the plug-thrust contribution, for isentropic expansion of hydrogen for the dissociated and/or ionized fraction held constant (frozen flow) at the pre-expansion conditions of temperature and pressure. Comparison of these data with earlier work• shows that the plug-thrust contribution is negligible for the expansion ratio considered.

*"High-Temperature Materials Program Progress Report No. 28, Part B," GE-NMPO, GEMP-28B, November 11, 1963, p. 39.

†"High-Temperature Materials Program Progress Report No. 30, Part B," GE-NMPO, GEMP-30B, December 31, 1963, p. 46.

‡ Ibid., p. 46.

§ R. Richter and L. Cumber, GE-MSD.

• K. E. Kissell, "Thermodynamic Performance Study of Possible Working Fluids for Non-Chemical Rockets," *Planetary Space Science*, Vol. 4, 1961, pp. 111-132.

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Fig. 4.3-2—Variation in hydrogen specific impulse with pre-expansion total temperature for selected nozzle pressure ratios and energy conversion processes

Data for equilibrium isentropic expansion* (the molecular and/or dissociated fractions are assumed to be in true equilibrium at each temperature and pressure extant during the nozzle expansion) are presented in Figure 4.3-2 to indicate an upper limit to the specific impulse attainable via isentropic expansion of hydrogen. In practice, true equilibrium expansion cannot be attained due to the low recombination rates of dissociated and/or ionized hydrogen relative to the fluid dwell time at any station along the nozzle.† Therefore, future analyses will assume frozen-flow expansion when considering isentropic flow.

Isothermal‡ expansion has been identified as a theoretical means of obtaining higher specific impulses, relative to isentropic expansion, at the same propellant temperatures.§ The contained-fission GCR may be applicable to this process since it may be possible to position a portion of the transparent container to permit energy addition to the propellant during the expansion process. The degree to which isothermal expansion might be approached in this system is not presently known. Furthermore, the only analysis of this process has been accomplished in terms of a perfect gas. Based upon the work of Winter-

*B. M. Rosenbaum and L. Levitt, "Thermodynamic Properties of Hydrogen from Room Temperature to 100,000°K," Lewis Laboratories, NASA TN D-1107, January 1962.

†W. G. Browne, "Chemical Recombination in Hydrogen Mixtures During an Expansion," GE-FPD, R 61 FPD, May 1961, p. 272.

‡Constant static temperature.

§F. Winterberg, "Die Erreichung von Ausstromgeschwindigkeiten bis 20,000 m/s durch Isothermal Expansion in Kernraketen," IXth International Astronautical Congress, Amsterdam, 1958.

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berg or the influence coefficients of Shapiro,* the specific impulse for isothermal expansion, including the plug-thrust contribution, is given by the equation:

$$I_{sp} = \sqrt{\frac{T_c}{m}} \left\{ \sqrt{\frac{R}{g} \left(\frac{k M_c^2}{a} + 2 \ln b \right)} + \sqrt{\frac{R}{kg}} \left(\frac{1}{M_c} \right) a^x \right. \\ \left. \frac{P_e}{P_c} \exp \left[a \ln b - \frac{1}{2} \ln \left(1 + \frac{2a}{k M_c^2} \ln b \right) \right] \right\} \quad (4.1)$$

where

$$a = 1 + \frac{k-1}{2} M_c^2$$

$$b = \frac{P_c}{P_e a \exp \left(\frac{k-1}{k} \right)}$$

T_c = pre-expansion total temperature, °R

m = average pre-expansion molecular weight, lb/lb-mole

R = universal gas constant, ft-lb/lb-mole-°R

k = pre-expansion ratio of specific heat

P_e = nozzle exit static pressure, atm

P_c = pre-expansion total pressure, atm

M_c = pre-expansion fluid Mach number

g = gravity constant, ft/sec²

$$x = \frac{k+1}{2(k-1)}$$

This may be approximated by the relation

$$I_{sp} = \sqrt{\frac{T_c R}{m g}} \left(\sqrt{2 \ln \left(\frac{P_c}{P_e} \right)} + \frac{1}{M_c} \frac{P_e}{P_c} \frac{1}{\sqrt{k}} \exp \left\{ \ln \frac{P_c}{P_e} \right. \right. \\ \left. \left. - \frac{1}{2} \ln \left[1 + \frac{2}{k M_c^2} \ln \left(\frac{P_c}{P_e} \right) \right] \right\} \right) \quad (4.2)$$

when the pre-expansion Mach number is small. The data of Figure 4.3-2 for isothermal expansion based upon this equation and the hydrogen property data of Rosenbaum illustrate the theoretical advantage of this expansion process over isentropic expansion and also the sensitivity of isentropic expansion to nozzle pressure ratio. This sensitivity is due, in part, to the variation in the plug-thrust contribution with nozzle area ratio but is primarily the result of the exit velocity dependence on the root of the natural logarithm of the nozzle pressure ratio. Although the accuracy of the perfect gas model remains to be determined, it should be good since the isothermal expansion automatically precludes the need for consideration of recombination of dissociated and/or ionized hydrogen. Furthermore, if the hydrogen is not yet fully dissociated at the temperature extant at the start of the expansion process, the completion of dissociation may occur due to the decreasing pressure with constant (static) temperatures, and thereby increase the impulse over that predicted by the perfect gas model.

Limitations on Attainable Specific Impulse of the Contained-Fission GCR Rocket

Data for specific impulse of hydrogen versus hydrogen temperature (Figure 4.3-2) permit delineation of the effects of two basic physical phenomena which are significant in

*A. Shapiro, "The Dynamics and Thermodynamics of Compressible Fluid Flow," Vol. I, Ronald Press, New York, 1953.

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limiting the ultimate performance, in terms of specific impulse, of GCR rockets transmitting energy by thermal radiation through a transparent wall. These are (1) container wall transparency, which decreases markedly in the ultraviolet portion of the electromagnetic spectrum for all identified materials for which measurements have been made and (2) the deposition of energy in solid components of the reactor in relation to the total energy generated. Wall transparency limits are unique to contained-fission GCR while solid component energy deposition limits are common to all identified GCR nuclear rocket concepts.

The specific impulse limits imposed by these effects are, to a lesser degree, also a function of the nozzle flow process employed to convert the propellant thermal energy to kinetic energy. Figure 4.3-3 presents two sets of data. The first is the variation in the unique wavelength associated with the energy peak in the black body spectrum at a particular temperature with the hydrogen specific impulse attainable at that temperature ($\lambda_{\max} T = 0.290 \text{ cm}^\circ\text{K}$). The second set of curves in this figure presents the

Fig. 4.3-3—Evaluation of black body spectrum and solid component cooling requirements versus specific impulse

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variation of the fraction of the energy required to heat the hydrogen to 5000°R relative to the total energy required to heat the hydrogen to a particular temperature,* with the specific impulse attainable at that temperature. The 5000°R temperature is representative of the maximum allowable temperature of regeneratively cooled reactor components. Although this value may be optimistic, it is consistent with another study.† Well-defined regions, e. g., visible, ultraviolet, etc., of the electromagnetic spectrum are delineated in Figure 4.3-3 (with respect to the left ordinate). Isothermal expansion as well as frozen and equilibrium isentropic expansion are considered. A chamber pressure of 100 atmospheres and a nozzle pressure ratio of 1000 are employed.

Conclusions permitted by this study with respect to the contained fission GCR are twofold. The first is that specific impulses in excess of 3000 seconds are currently prohibited by both the ultraviolet transparency limit and the allowable solid component heating fraction. Consequently, it is desirable to identify or investigate development of a material transparent in the ultraviolet range. This guideline forms the basis for the identification of new materials for compatibility testing with potential nuclear fuels. Furthermore, design concepts must be identified to reduce the penalty associated with solid component secondary heating limitations. This aspect applies to all identified types of GCR nuclear rockets.

The second conclusion permitted from the data of Figure 4.3-3 is that, within the limits imposed by ultraviolet and solid component heating, the highest specific impulses are theoretically permitted by the use of isothermal expansion.

Effects of Nuclear Fuel Pressure Level

Conceptually, the mechanical stresses in the transparent container material can be eliminated by equating the nuclear fuel pressure level within the container and the propellant pressure level outside the container. This concept requires a pressure vessel external to the neutron reflector to absorb the mechanical stresses. A preliminary analysis of nuclear fuel pressure levels has been completed and was based upon critical mass requirements of the GCR as a function of core diameter for a 100-centimeter graphite reflector. This evaluation does not investigate hydrogen pressure level requirements as a function of seeding material concentration‡ necessary to provide hydrogen opacity to thermal radiation.

Computation of nuclear fuel pressure levels for a given reactor and temperature requires data for nuclear fuel inventory requirements. Estimated U²³⁵ critical mass requirements are presented in Figure 4.3-4 as a function of active core diameter and graphite reflector thickness. These data are for equilateral right cylinder geometries and are based on the geometric buckling analogy of Hyland§ as applied to the computer analysis of spherical geometry cavity reactors of MacLain.¶ The computer analysis of spherical cavity reactors provides a particular fuel loading for each active core diameter and reflector thickness. Under the assumption that material densities are equal in both the

*Rosenbaum, loc. cit.

†R. G. Ragsdale, "Performance Capability of Single Cavity Vortex Gaseous Nuclear Rockets," NASA, Lewis Laboratories, TN D-1579, May 1963.

‡C. D. Lanzo and R. G. Ragsdale, "Experimental Determination of Spectral and Total Transmissivities of Clouds of Small Particles," NASA, Lewis Laboratories, TN D-1405, September 1962.

§R. E. Hyland, et al., "Two Dimensional Criticality Calculations of Gaseous-Core Cylindrical-Cavity Reactors," NASA, Lewis Laboratories, TN D-1575, March 1963.

¶R. I. MacLain, "Observations on the Nuclear Properties of U-235 Fueled Cavity Reactors," Dept. of Engineering, University of California at Los Angeles, July 1962.

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Fig. 4.3-4—Equilateral ($L/D = 1.0$) cylindrical reactor U^{235} inventory requirements versus core diameter as a function of reflector thickness

spherical and cylindrical systems, the inventory of the cylindrical system may be obtained from the relation

$$\left(\frac{W}{4/3 \pi r_0^3} \right)_{\text{spherical}} = \left(\frac{W}{2\pi r_0^3 \frac{L}{D}} \right)_{\text{cylindrical}}$$

where

W = U^{235} inventory, kg

r_0 = core radius

L/D = cylindrical core length-to-diameter ratio

subject to the geometric buckling relationship

$$\left(\frac{\pi}{R_s} \right)^2 = \left(\frac{2.405}{R_c} \right)^2 + \left(\frac{\pi}{H_c} \right)^2$$

where

R_s = nuclear radius of the spherical reactor

R_c = nuclear radius of the cylindrical reactor

H_c = nuclear height of the cylindrical reactor

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With the available computer code, running times for GCR with a radius greater than 40 centimeters are excessive.* Inventory requirements for cylindrical reactors have been assumed to lie between the two limiting cases imposed by the radius of the core and the radius of the reactor; that is,

$$\text{for } \begin{cases} R = r_0 \\ H = 2 r_0 L/D \end{cases} \text{ and } \begin{cases} R = r_0 + t_R \\ H = 2 (r_0 L/D + t_R) \end{cases}$$

t_R = reflector thickness

This analysis then implies that if a radius exists such that the geometric bucklings of the spherical and cylindrical systems may be equated, this radius lies between the cavity radius and the reactor radius.

This analysis results in the two sets of data presented for each reflector thickness in Figure 4.3-4. The inventory requirements shown are almost twice those required for C^{12} reflected, U^{235} fueled cavity reactors. This results from effects summarized in Table 4.3-1. It is noted that the effect of nuclear fuel temperature is uncertain and is not included. MacLain predicts an increase in U^{235} inventory by a factor of approximately 2.0 when nuclear fuel temperature increases from 20°C to 3000°C while Hyland predicts a decrease by a factor of 1.7 for the same conditions.

TABLE 4.3-1
ESTIMATED PERTURBATIONS
ON U^{235} INVENTORY REQUIREMENTS
OF C^{12} REFLECTED CYLINDRICAL CAVITY REACTORS

Condition	Relative Inventory Of U^{235}
U^{235} fueled, C^{12} reflected cavity at 20°C^a	1.0
Change C^{12} to reactor-grade graphite	1.7
Change from 100% to 90% solid graphite ^b	1.35
Change from U^{235} to $U^{235} + F-19$ F/U = 7.1 ^c	0.85
Change from 100% to 93% enrichment	negligible
Product of all changes	1.95 ^a

^aEffect of temperature change is uncertain and is not included.

^bImposed here to provide some allowance for eventual coolant passage requirements.

^cF/U atom ratio of 6 was used in pressure level calculations.

The minimum inventory requirements of Figure 4.3-4 for a 100-centimeter graphite reflected system have been employed to provide a preliminary assessment of the nuclear fuel pressure level encountered in the contained-fission GCR. The results of this study are shown in Figure 4.3-5,[†] which presents an iron gamma-shadow-shielded rocket engine thrust-to-weight ratio versus active core diameter as a function of thrust level, surface black body nuclear fuel temperature, and average nuclear fuel pressure based upon this temperature. Assumptions present in this analysis are:

1. An isentropic frozen flow specific impulse of 1500 seconds requiring a 100-atmosphere hydrogen temperature of $10,600^\circ\text{R}$ at a nozzle pressure ratio of 1000 (Figure 4.3-2).

*Hyland, loc. cit.

[†]Figure 6.1 (GEMP-28B) and Figure 6.2 (GEMP-30B) utilized an infinite nozzle pressure ratio permitting complete recovery of propellant thermal energy. This unrealistic condition has been removed on Figure 4.3-5 of this report by the assumption of a finite nozzle pressure ratio.

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Conditions:

 $I_{sp} = 1500$ Seconds; $T_{Hydrogen} = 10,600^{\circ}R$ (max); $P_{Hydrogen} = 100$ Atmosphere (P_c) $P_c/P_e = 1000$; Frozen Isentropic ExpansionNuclear fuel pressure based upon inventory of Figure 4.3-4 as fully dissociated UF_6 (minimum for 100-cm graphite reflector)

Fig. 4.3-5—Iron gamma shadow shielded GCR rocket engine thrust-to-weight ratio versus active core diameter as a function of net thrust and nuclear fuel temperature and pressure

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2. Geometry: core-equilateral cylinder; radiation heat transfer area is equal to that of side and rear of core only.
3. Nuclear fuel as UF_6 is fully dissociated to free atoms.
4. System weight is that of reflector, pressure shell, and iron gamma shadow shield.
5. Gamma shadow shielding limits total gamma dose to 25 roentgens per mission for 100-foot separation.
6. Effects of nuclear fuel temperature and lack of rear reflector on inventory requirements are neglected.

The deviation from the separation of variables previously reported* is necessary to provide a particular set of geometry and nuclear fuel temperature conditions upon which the nuclear fuel inventory and therefore pressure may be based. The data of Figure 4.3-5 will vary as a reactor arrangement is altered and as other nozzle energy conversion processes are considered. The nuclear fuel pressure levels are also subject to more accurate determination of inventory requirements, particularly as affected by the reactor temperature coefficient. No conclusions are drawn at this time because of the preliminary nature of this study. The techniques developed for, and the guidance provided by this analysis are necessary in the analysis of container material heating rates since the nuclear fuel pressure and temperature are required to determine its optical and thermal properties.

Container Thermal Heating Rate Studies

Work initiated on container thermal heating by conduction indicates that the simplest model for the analysis of these effects requires determination of the thermal gradients in the nuclear fuel due to conduction and radiation as a function of radius. At some radius the gradient due to radiation heat transfer will equal that due to pure conduction. The ratio of the heat conducted by the nuclear fuel, at this radius, to that radiated will provide an initial estimate of container conductive heating.

An analysis of stellar environments† has been investigated to obtain guidance as to the temperature distribution extant in a radiating gas. The results of this work demonstrate that a knowledge of the optical thickness of the radiating gas is necessary to assess its temperature distribution. This parameter, in conjunction with the thermal conductivity of the nuclear fuel will permit the preliminary evaluation of the wall heating by thermal conduction as a function of the total radiation energy transfer requirement dictated by that of the rocket engine. Therefore, as a minimum, evaluation of this effect requires determination of the thermal conductivity and the optical thickness of the nuclear fuel. The optical thickness is in turn dictated by the radiative properties of the nuclear fuel, particularly its spectral emissivity.

SUMMARY AND CONCLUSIONS

The experimental apparatus for working with UF_6 was completed and corrosion tests with this material were initiated. In another apparatus, testing of Al_2O_3 and MgO in contact with UCl_4 at 1000°C is in progress.

A computer program to determine the thermodynamic functions of gases by statistical mechanical calculations was written and is being checked.

The thermal and nuclear studies have established preliminary generalizations linking nuclear rocket performance and container materials environment.

*"High-Temperature Materials Program Progress Report No. 30, Part B," GE-NMPO, GEMP-30B, December 31, 1963, p. 46.

†V. A. Ambartsumyan, "Theoretical Astrophysics," Pergamon Press, Inc., New York, 1958

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PLANS AND RECOMMENDATIONS

Corrosion tests with UF_6 and with other uranium halides will be continued.

Thermodynamic calculations will be continued, directed toward specifying the equilibrium composition of the gaseous atmosphere of the reactor core.

In the thermal and nuclear studies, work will be initiated on the optical properties of the nuclear fuel. Due to the overall complexity of the wall thermal heating analysis, the feasibility of developing a single model to account for the combined effects of radiation conduction and convection will be investigated. This study is desirable if only to establish all the variables of the total problem.

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APPENDIX

REPORTS ISSUED DURING CALENDAR YEAR 1963

PROGRESS REPORTS

GEMP-177A

Second Annual Report - High-Temperature Materials and Reactor Component Development Programs, Volume I - Materials, February 28, 1963.

GEMP-177B

Second Annual Report - High-Temperature Materials and Reactor Component Development Programs, Volume II - Materials, February 28, 1963.

GEMP-177C

Second Annual Report - High-Temperature Materials and Reactor Component Development Programs, Volume III - Reactor Component Development, February 28, 1963.

METALLURGY

GEMP-19A and B

High-Temperature Materials Program Progress Report No. 19, January 25, 1963.

GEMP-21A and B

High-Temperature Materials Program Progress Report No. 21, April 23, 1963.

GEMP-23A and B

High-Temperature Materials Program Progress Report No. 23, May 31, 1963.

GEMP-25A and B

High-Temperature Materials Program Progress Report No. 25, July 31, 1963.

GEMP-27A and B

High-Temperature Materials Program Progress Report No. 27, September 30, 1963.

GEMP-29A and B

High-Temperature Materials Program Progress Report No. 29, November 30, 1963.

CERAMICS

GEMP-22A and B

High-Temperature Materials Program Progress Report No. 22, April 30, 1963.

GEMP-24A and B

High-Temperature Materials Program Progress Report No. 24, June 28, 1963.

GEMP-26A and B

High-Temperature Materials Program Progress Report No. 26, August 16, 1963.

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High-Temperature Materials Program Progress Report No. 28, November 11, 1963.

GEMP-30A and B

High-Temperature Materials Program Progress Report No. 30, December 31, 1963.

INSTRUMENTATION AND CONTROLS

GEMP-76

Reactor Instrumentation and Control Progress Report No. 76, April 29, 1963.

GEMP-77

Reactor Instrumentation and Control Progress Report No. 77, May 31, 1963.

GEMP-78

Reactor Instrumentation and Control Progress Report No. 78, July 31, 1963.

GEMP-79

Reactor Instrumentation and Control Progress Report No. 79, September 30, 1963.

GEMP-80

Reactor Instrumentation and Control Progress Report No. 80, November 30, 1963.

TOPICAL REPORTS

C. S. Wukusick, "Oxidation Behavior of Intermetallic Compounds in the Nb-Ti-Al System," GE-NMPO, GEMP-218, July 1963.

J. F. White, E. F. Juenke, and D. R. Burgbacher, "The $\text{UO}_2\text{-UO}_3\text{-Y}_2\text{O}_3$ System and Evaluation of the $\text{UO}_{2.9}\cdot 3\text{Y}_2\text{O}_3$ Composition," GE-NMPO, GEMP-263, (to be published).

D. G. Besco and J. R. Beeler, Jr., "Computer Programs Describing Collision Cascades in Binary Materials, I: Square Planar Lattice," GE-NMPO, GEMP-192, February 1963.

E. C. Duderstadt and J. F. White, "The Sintering of BeO to Variable Densities and Grain Sizes," GE-NMPO, GEMP-219, September 1963.

J. R. Beeler, Jr., "High-Speed Computer Experiment Techniques: Many-Particle Systems," GE-NMPO, GEMP-252, December 1963.

D. G. Besco and J. R. Beeler, Jr., "Computer Programs Describing Collision Cascades in Binary Materials, III: Body-Centered Cubic and Face-Centered Cubic Structures," GE-NMPO, GEMP-243, August 1963.

D. G. Besco and J. R. Beeler, Jr., "Computer Programs Describing Collision Cascades in Binary Materials, II: Wurtzite Structure," GE-NMPO, GEMP-200, February 1963.

J. A. Delaney, "Pseudo Infinite Lattices in a Digital Computer," GE-NMPO, GEMP-193, February 1963.

J. C. Drake, H. J. Kurtz, and R. L. Sundin, "Problems Associated with High Temperature Fasteners," GE-NMPO, GEMP-186, April 15, 1963.

INVENTION DISCLOSURES

There were nineteen invention disclosures resulting from the High-Temperature Materials Program and five from the Instrumentation and Controls Program at GE-NMPO.

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- J. F. White and A. L. Clavel, "Extrusion Properties of Non-Clay Oxides," Bull. Am. Ceram. Soc., Vol. 42, No. 11, 1963, pp. 698-702.
- L. H. Sjodahl and B. A. Chandler, "Single Crystal Elastic Constants of BeO from Polycrystalline Measurements," J. Am. Ceram. Soc., Vol. 46, No. 7, 1963, pp. 351-352.
- L. H. Sjodahl, "Orientation in Extruded BeO," GE-NMPO, TM 63-4-1. Submitted to J. Nuc. Matls.
- S. F. Bartram, E. F. Juenke, and E. A. Aitken, "Phase Relationships in the UO_2 - UO_3 - Y_2O_3 System," GE-NMPO, TM 63-7-14. To be published in J. Am. Ceram. Soc.
- E. A. Aitken, S. F. Bartram, and E. F. Juenke, "Crystal Chemistry of the Rhombohedral $\text{MO}_3 \cdot 3\text{R}_2\text{O}_3$ Compounds," Basic Science Division, American Ceramic Society Meeting, Washington, D. C., October 8, 1963, GE-NMPO, TM 63-10-2. Submitted to Inorganic Chemistry.
- R. E. Fryxell and B. A. Chandler, "Creep, Strength, Expansion, and Elastic Moduli of Sintered BeO as a Function of Grain Size, Porosity, and Grain Orientation," American Ceramic Society Meeting, Pittsburgh, Pennsylvania, April 30, 1963, GE-NMPO, TM 63-5-4. Submitted to J. Nuc. Matls.
- C. S. Wukusick and J. F. Collins, "Properties of Fe-Cr-Al Type Alloys Containing Additions of Yttrium," ASTM Subcommittee on Resistance Heating Materials Meeting, Atlantic City, N.J., January 25, 1963, GE-NMPO, TM 63-7-63. Submitted to ASTM Materials Research and Standards.
- E. A. Aitken, H. C. Brassfield, and J. A. McGurty, "Characteristics of Substoichiometric Urania," American Nuclear Society Meeting, Salt Lake City, Utah, June 1963, GE-NMPO, TM 63-2-14.
- E. A. Aitken, "Fuel Oxides," American Nuclear Society Meeting, Cincinnati, Ohio, April 1963, GE-NMPO, TM 63-4-13.
- C. G. Collins, "Radiation Effects in BeO," International Conference on Beryllium Oxide, Sidney, Australia, October 1963, GE-NMPO, TM 63-10-12.
- B. A. Chandler and J. B. McConnelee, "Thermal Stress Evaluation of Ceramic Fuel Elements," GE-NMPO, TM 63-4-2. Submitted to J. Nuc. Matls.
- E. S. Funston, W. J. Kirkpatrick, and P. P. Turner, "Preparation of High Purity BeO Powder," GE-NMPO, TM 63-4-8. Submitted to J. Nuc. Matls.
- J. R. Beeler, Jr., and D. G. Besco, "Range and Damage Effects of Tunnel Trajectories in a Wurtzite Structure," J. Appl. Phys., Vol. 34, 1963, p. 2873.
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