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GEMP-58B
AEC RESEARCH AND
DEVELOPMENT REPORT
MASTER

Nuclear Materials & Propulsion Operation

HIGH-TEMPERATURE MATERIALS PROGRAM PROGRESS REPORT No. 58, Part B

April 29, 1966

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C-44A Nuclear Technology -
Materials (M-3679) (44th Ed.)

**HIGH-TEMPERATURE MATERIALS PROGRAM
PROGRESS REPORT No. 58, Part B**

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SEP 20 1973

United States Atomic Energy Commission

Contract No. AT (40-1)-2847

**NUCLEAR MATERIALS and PROPULSION OPERATION
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CONVERSION TABLE

To Convert From	To	Multiply By
Atmospheres	Pounds/inch ²	14.7
Calories (mean)	Btu (mean)	0.00397
Calories/gram-°C	Btu/pound-°F	1.0
Calories/sec-cm-°C	Btu/hr-ft-°F	241.8
Calories/sec-cm ²	Btu/hr-ft ²	1.32 x 10 ⁴
Calories/sec-cm ² -°C	Btu/hr-ft ² -°F	7370
Centimeters	Feet	0.03281
	Inches	0.3937
Cubic centimeters	Cubic feet	3.531 x 10 ⁻⁵
	Cubic inches	0.06103
Grams	Pounds	0.002205
Grams/cm ³	Pounds/ft ³	62.43
Grams/cm ²	psi	0.01422
Kilograms	Pounds	2.205
Kilograms/cm ²	Atmospheres	0.9678
	Pounds/ft ²	2048
	Pounds/inch ²	14.22
Kilograms/mm ²	Pounds/inch ²	1422.32
Kilowatts	Btu/sec	0.948
Liters	Cubic feet	0.0353
Meters	Inches	39.37
Millimeters of mercury	Atmospheres	0.001316
Square centimeters	Square feet	0.001076
	Square inches	0.155
Torr	mm of Hg	1.0
	Atmospheres	0.001316
Watts/cm-°C	Btu/hr-ft-°F	57.8
Watt-seconds	Btu	0.000948
Watts/cm ²	Btu/hr-ft ²	3170
Watts/cm ² -°C	Btu/hr-ft ² -°F	1760
Centimeters/sec	Feet/sec	0.03281
Meters/sec	Feet/sec	3.281

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1. INTRODUCTION AND SUMMARY

Introduction

This report is the classified portion of the fifty-eighth in a series of monthly reports of the work in process on materials research and development for the Atomic Energy Commission under Contract AT(40-1)-2847.

Included is a summary of the work from February 1, 1966 to March 15, 1966, on three of the specific research and development efforts in process. Seven of the remaining programs are reported in the unclassified portion of this report, GEMP-58A.

Seven other research and development efforts covered by the contract are reported in alternate months.

Summary

BURNUP CAPABILITY OF Y_2O_3 -STABILIZED UO_2 AND BeO-STABILIZED FUEL MATERIALS (57068)

The last four static irradiation tests of this program were terminated as planned at the end of ETR cycle 78. Burnup densities calculated for these tests ranged from 2.1 to 5×10^{20} fissions/cm³ of total fuel element (8.4 to 34.9×10^{20} fissions/cm³ fuel phase). Control tests operated for equivalent times and temperatures were completed in support of these irradiation tests and showed no significant changes in weight, dimensions, or strength.

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

Vapor pressures for $UO_{1.88}$ and $UO_{1.96}$ over the temperature range from 2100° to 2600°C were calculated from transpiration measurements. For each composition, a temperature dependency was followed which agreed with that extrapolated from lower temperature data for $UO_{2.00}$. For $UO_{1.96}$, the vapor pressures were 0.014 and 1.4 mm of Hg at 2100° and 2600°C, respectively. The values for $UO_{1.88}$ were about a factor of three greater than for $UO_{1.96}$.

Diffusion couples of UO_2 and ThO_2 were studied by electron microprobe techniques over the temperature range from 1800° to 2500°C. Interdiffusion coefficients were calculated which agree with self-diffusion coefficients of uranium in UO_2 as extrapolated from lower temperature measurements.

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Microstructural evaluation provides evidence of considerable interaction of Ta and UO_2 after extended tests of Ta-encapsulated UO_2 specimens in hydrogen at temperatures of 2150°C and above.

Microstructural evaluation of Ta-encapsulated UO_2 specimens which were thermal cycled between 2150° and 260°C in helium shows evidence of accumulative UO_2 entry into the Ta and some Ta contamination of the UO_2 when the oxygen content of the total system is maintained at the initial value by a Re envelope around the specimen.

Rhenium-encapsulated W- $\text{UO}_{2.00}$ tested in argon under thermal gradient conditions for 70 hours did not show evidence of a concentration gradient in the UO_2 .

HIGH-TEMPERATURE RESEARCH ON CARBIDES FOR FUEL AND STRUCTURAL APPLICATIONS (57073)

Further gas – solid equilibrium experiments to determine carbon activity as a function of composition were completed at carbon activities between 0.001 and 0.01 at 1800°C and 2150°C.

The expression relating the carbon activity coefficient to the carbon interaction energies in TaC_x was found to be:

$$Rt \ln \left(a_c \frac{1-x}{x} \right) = -50.6 + (36.6 \pm 4.7) x - (4.4 \pm 1.1) 10^{-3} T$$

Tests using dried or undried H_2 as the test atmosphere at 2150°C showed that traces of water vapor can have an effect upon the lattice parameter of TaC_x , particularly when the water vapor is present in quantities equivalent to the quantity of carbon present in the test atmosphere. This effect can lead to erroneous estimates of composition.

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2. BURNUP CAPABILITY OF Y_2O_3 -STABILIZED UO_2 AND BeO-STABILIZED FUEL MATERIALS

(57068)

The objective of this program is to determine the effect of high fuel burnup on stabilized fuel systems as such and as sources of fuel in BeO-base fuel elements.

IRRADIATION TESTING

The in-pile portion of this program was completed with the termination of static irradiation tests 33MT-123 (Y_2O_3 -stabilized ZrO_2 -coated 15BF-216), 33MT-124 (BeO-coated UO_{2+x} $3Y_2O_3$), GEFP2-19 (11.5BF-230), and GEFP2-22 (BeO-coated 6BF-243). The first three of these tests operated at the equivalent of full reactor power for 6005 hours and the last test for 3505 hours. Calculated burnups (total fuel element and fuel phase only) are shown in Table 2.1. The calculated fuel phase burnup of 34.9×10^{20} fissions/cm³ for test 33MT-123 was the highest fuel phase burnup attained in this program; the calculated total fuel element burnup of 5×10^{20} fissions/cm³ for test GEFP2-19 was the highest total fuel element burnup attained. Examination of the outer hardware of the cartridges after removal from the ETR showed no detrimental effects as a result of irradiation.

Control Testing

Non-nuclear testing of control specimens in support of completed irradiation tests 33MT-123, 33MT-124, GEFP2-19, and GEFP2-22 was completed and the results are shown in Table 2.1. Weight change measurements showed a small increase which was attributed to oxidation of the fuel phase. Volume change calculated from density measurements showed a decrease for all tests and was attributed to shrinkage caused by the extended heat treatment. Strength changes determined from modulus-of-rupture measurements ranged from a 5 percent loss to a 26 percent gain. There were no significant changes in dimensions in any of the control tests.

Post-Irradiation Evaluations

During this report period, post-irradiation evaluations were limited to examination of ceramography samples and electron microscope replicas from previously completed irradiation tests. Because of polishing problems, the structure of most of the samples was difficult to define and new polishing techniques are being explored to permit a more complete evaluation of these samples. The electron microscope replicas from fracture surfaces were also difficult to evaluate because the structure of the fuel phase and the BeO phase appears to be identical; however, gas bubbles were found. Replication of polished surfaces will be done in an attempt to resolve the problem of identifying the phases in these fuel element samples. Replication of fracture surfaces that had been

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TABLE 2.1
IRRADIATION TEST PROGRAM FOR HIGH BURNUP AT 1250°C

EXPERIMENTAL TEST PROGRAM FOR HIGH BURNUP AT 1200 °C																
Test Number	Specimen Designation	Coating ^a	Specimen Composition, ^b			Operating Conditions		Burnup,		Kr ⁸⁵ ^d Fraction Released	Weight Change ^e Of Irradiated Specimens, %	Length Change ^e Of Irradiated Specimens, %	Strength Change, %		Volume Change, %	
			wt %			Time, hr	Average Temperature, °C	10 ²⁰ fissions/cm ³					Control	Irradiated	Control	Irradiated
			Fuel	Additive	BeO			Total Fuel Element ^c	Fuel Phase Only ^c							
33MT-84 ^f	20BF-204Gd	None	20.18	45.9	54.1	1688	1370	1.45	5.5		-1.0 (3) ^g	+0.7 (3)	+2.0 (4)	-22 (1)	-1.5	+0.9 (3)
33MT-109	20BF-204	Y ₂ O ₃ -stab. ZrO ₂	20.50	47.7	52.3	2604	1215	2.06	7.5	1.9 x 10 ⁻¹	-0.1 (1)	+1.2 (1)	-20 (3)	-49 (3)	-0.4	+6.0 (2)
33MT-114	20BF-204	Y ₂ O ₃ -stab. ZrO ₂	20.50	47.7	52.3	1601	1370	1.75	6.4	1.6 x 10 ⁻⁴	+0.7 (2)	+0.9 (3)	+2.5 (2)	-38 (3)	-0.9	+4.3 (3)
33MT-120	9.5BF-204	Y ₂ O ₃ -stab. ZrO ₂	9.67	22.5	77.5	2086	1170	0.89	8.2	6.2 x 10 ⁻³	-0.3 (2)	+0.6 (2)	+18 (3)	-28 (2)	-1.0	+0.6 (2)
33MT-121	9.5BF-204	Y ₂ O ₃ -stab. ZrO ₂	9.67	22.5	77.5	1601	1305	0.87	8.0	2.6 x 10 ⁻²	-0.3 (3)	+0.7 (3)	+10 (3)	- 8 (3)	-0.5	+2.0 (3)
33MT-117	20BF-216	Y ₂ O ₃ -stab. ZrO ₂	20.22	31.9	68.1	2344	1190	2.01	13.7	9.2 x 10 ⁻⁴	h	h	+43 ^h (3)	-32 ^h (3)	-0.4	+2.9 (2)
33MT-118	20BF-216	Y ₂ O ₃ -stab. ZrO ₂	20.22	31.9	68.1	1601	1365	1.09	7.5	1.2 x 10 ⁻²ⁱ	-0.6 (2)	+0.7 (2)	-17 (2)	+2.0 (2)	-0.5	+5.5 (2)
33MT-123	15BF-216	Y ₂ O ₃ -stab. ZrO ₂	15.10	23.8	76.2	6005	1220	3.6 ^j	34.9 ^j	—	—	—	- 5 (3)	—	-0.6	—
33MT-125	15BF-216	Y ₂ O ₃ -stab. ZrO ₂	15.10	23.8	76.2	1242	1095	1.0 ^j	9.7 ^j	3.1 x 10 ⁻²	+0.3 (3)	+0.8 (2)	- 1 ^h (3)	-45 ^h (4)	-0.6	+2.9 (3)
33MT-124	UO _{2+x} ·3Y ₂ O ₃	BeO	Inhomogeneous fuel ^k			6005	1035	2.3 ^j	25.0 ^j	—	—	—	- 1 (3)	—	-0.2	—
33MT-126	UO _{2+x} ·3Y ₂ O ₃	BeO	Inhomogeneous fuel ^k			2960	1160	1.6 ^j	17.4 ^j	4.8 x 10 ⁻¹	-4.4 (3)	<-0.1 (1)	-22 ^h (2)	+25 ^h (2)	-0.1	m
GEFP2-19	11.5BF-230	None	11.57	50.4	49.6	6005	1215	5.0 ^j	20.0 ^j	—	—	—	+26 ^q (3)	—	-1.0	—
GEFP2-22	6BF-243	BeO	6.20	51.5	48.5	3505	1125	2.1 ^j	8.4 ^j	—	—	—	+2.8 (3)	—	-0.7	—
GEFP2-23	11.5BF-230	None	11.57	50.4	49.6	4116	1170	3.6 ^j	14.4 ^j	n	-0.10 (3)	+1.4 (3)	+24 (3)	-22 (3)	-0.2	+3.3 (3)
LTC-72	UO _{2+x} ·3Y ₂ O ₃	BeO	Inhomogeneous fuel ^k			303	855 – 1205	p	p	—	+0.02 (6)	0 (6)	+50 (8)	-7.9 (6)	-0.5	0 (6)
LTC-73	11.5BF-230	None	11.57	50.4	49.6	931	1250 – 1550	p	p	—	-0.3 (6)	+0.5 (6)	0 (6) ^h	-28 ^h (6)	-0.06	+1.8 (6)
LTC-74	11.5BF-230	BeO	11.57	50.4	49.6	817	1250 – 1500	p	p	—	0 (6)	0 (6)	-2.5 (6)	-27 ^h (12)	-0.03	-1.0 (6)

^aY₂O₃-stabilized ZrO₂ coatings were vapor deposited, 0.0025 cm thick; BeO coating was applied to UO_{2+x}·3Y₂O₃ as a 0.005-cm dip-coat on the inside surface only. BeO was dip-coated on GEFP2-22 and LTC-74 specimens over the entire surface, 0.004 to 0.007 cm thick.

^bPercentages of UO₂ in BF compositions are from chemical analyses. 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.

	Fuel Additive Composition, wt %				
	UO ₂	ZrO ₂	Gd ₂ O ₃	Y ₂ O ₃	ThO ₂
F-204Gd	45	19.4	2.25	33.35	—
F-204	45	19.4	—	35.6	—
F-216	65	12.4	—	22.6	—
F-230	22.8	—	—	10.4	66.8
F-243	12.0	—	—	5.5	82.5

^c33MT-84 value is the average burnup of all three specimens by Cs¹³⁷ and Ce¹⁴⁴ analysis; 33MT-109, -114, -120, -121, -117, and -118 values are maximum values arrived at by adjusting U²³⁶/U²³⁵ mass spectrometer analyzed values by a percentage calculated from gamma scan results of the specimens before dissolution for burnup analysis.

^dAnalogous to R/B values calculated for dynamic in-pile tests.

^eSince all changes in weight and dimensions of the control specimens were insignificant, they are omitted. The length changes shown are representative of the dimensional changes occurring as a result of irradiation.

^fCartridge design shown in "High-Temperature Materials Program Progress Report No. 22, Part B," GE-NMPO, GEMP-22B, April 30, 1963, p. 33. All irradiation tests have been completed.

^gNumbers in parentheses are number of determinations used to calculate percentage change.

^hAll specimens from 33MT-117 were broken probably as a result of camber produced in the tubes during irradiation; no weight, length, nor 7.62-cm span modulus-of-rupture determinations could be made. Strength values were determined using 4.45-cm span. Strength values of LTC-73, LTC-74, 33MT-125, and 33MT-126 specimens were also determined using 4.45-cm span.

ⁱMinimum value. Based on estimates of the amount of Kr⁸⁵ lost in transfer, the fractional gas release was ~2.4 x 10⁻².

^jCalculated burnup values based on ETR flux.

^kUO_{2+x}·3Y₂O₃ was co-extruded as 0.0076-cm cladding on the inside surface of a BeO tube and subsequently dip-coated with 0.005-cm BeO.

^mVolume change calculated from density change is not valid for this test because of BeO hydrolysis loss.

ⁿFission gases were lost prior to puncturing; therefore, no release information will be obtained from this test.

^pBurnup not applicable; these were dynamic tests to determine fission product release kinetics.

^qThese data inadvertently obtained after 4116 hours of the control test. Other data obtained after 5000 hours at 1200°C indicate a gain in strength of 7 percent.

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leached to remove the fuel did not yield additional information compared with the unleached fracture surfaces.

WORK PLANNED FOR NEXT PERIOD

Post-irradiation evaluations will continue including fission gas collection and specimen evaluation of the last four static irradiation tests of this program. Work will continue on improving the quality of the polished surfaces of ceramography samples from previous irradiation tests. Evaluation of electron microscope replicas will also continue.

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3. 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.

PHYSICAL CHEMISTRY

Vapor Pressure of UO_{2-x}

As described previously,¹ a study of the vapor pressure of UO_{2-x} as a function of temperature above 2000°C and for x values of 0.04, 0.08, and 0.12 is being made. It was noted that (1) the vapor pressures calculated from weight loss data of previous experiments, assuming transpiration conditions, were in reasonable agreement with values obtained elsewhere; (2) the equipment was being refined by the addition of a strain-gage thermobalance for continuous monitoring of weight loss; (3) more accurate measurement of gas flow past the specimen was being made; (4) specimens of presumed congruent compositions (e. g., $\text{UO}_{1.88}$ at 2400°C in dry hydrogen) did not change in composition under the appropriate temperature - atmosphere conditions for rather broad variations in flow rates above or below the values generally used; and (5) the weight loss as a function of time was linear for a given flow rate and temperature.

To determine vapor pressure by weight loss, it is necessary to establish that the gas stream flowing past the specimens is saturated with all the vapor species originating with the specimen. The conventional method of establishing this condition is to determine the apparent vapor density of the transpired material as a function of carrier gas flow rate past the specimen. Transpiration conditions are then satisfied when the apparent vapor density is constant as a function of the flow rate (i. e., the plateau or inflection point of a vapor density versus flow rate curve).

Results of vapor pressure versus gas flow rate are shown in Figures 3.1 and 3.2 for five temperatures for each of two compositions, plotted logarithmically to present three orders of magnitude. Saturation conditions are realized for $\text{UO}_{1.88}$ at flow rates of from 800 to 2000 cm^3/min of hydrogen (through a tube of 2.5 cm diameter cross section). For $\text{UO}_{1.96}$ in an atmosphere of 95Ar - 5H₂, a significant plateau was not observed; the inflection point occurred at about 1600 cm^3/min and probably represents saturation conditions.

In Figure 3.3, the vapor pressures of $\text{UO}_{1.96}$ and $\text{UO}_{1.88}$ as a function of reciprocal temperature are compared with the data of Ackermann, Gilles, and Thorn (AGT)²: (1) the data extrapolated from the straight line portion of the AGT curve for temperatures below 2000°K, according to the equation $\log p_{\text{mm}} = -33115/T - 4.026 \log T + 25.686$; and (2) the

¹"Fifth Annual Report - High-Temperature Materials Programs, Part B," GE-NMPO, GEMP-400B, February 28, 1966, pp. 20-23.

²R. J. Ackermann, P. W. Gilles, and R. J. Thorn, "High-Temperature Thermodynamic Properties of Uranium Dioxide," *Journal of Chemical Physics*, Vol. 25, 1956, pp. 1089-1097.

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Fig. 3.1 - Apparent vapor pressure of $UO_{1.88}$ versus gas flow rate at various test temperatures

Fig. 3.2 - Apparent vapor pressure of $UO_{1.96}$ versus gas flow rate at various test temperatures

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Fig. 3.3—Vapor pressure of urania as a function of reciprocal temperature

actual AGT experimental values at the higher temperatures. The slopes of both curves representing the data in Figures 3.1 and 3.2 (for flow rates of 1600 cm³/min) parallel the extrapolated (AGT) curve; the UO_{1.96} curve being within a factor of 1.5 of the extrapolated curve. The vapor pressure of the UO_{1.88} species is shown to be approximately three times the vapor pressure of UO_{1.96} in the given temperature range (2100° to 2600°C) and to equal the AGT experimental values near 2300°C. The steeper slope of the AGT experimental curve at elevated temperatures probably results from changing stoichiometry during the measurements under vacuum conditions.

Studies of UO₂-ThO₂ Solid Solutions

In previous studies of UO₂-ThO₂ solid solutions, appreciable differences were observed in the diffusivities of uranium and thorium.³ For example, pore development and swelling

³"Fifth Annual Report—High-Temperature Materials Programs, Part B," GE-NMPO, GEMP-400B, February 28, 1966, pp. 27–30.

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of compacts was related to the preferential movement of the UO_2 in agglomerates into the surrounding UO_2 - ThO_2 phase. The experimental results did not establish definitely the controlling interdiffusion mechanism. Therefore, further study was undertaken to determine the interdiffusion behavior in the solid-state reaction between UO_2 and ThO_2 .

The initial experiments involved reaction between couples of sintered compacts of UO_2 and ThO_2 . The density of the compacts was greater than 97 percent of theoretical. The compacts, approximately 10 mm in diameter and 4 to 5 mm thick, were ground and polished flat on the mating surfaces. A very thin dispersed layer of fine tungsten powder was placed on the surface of the ThO_2 compact to mark the original interface. The UO_2 compact was placed on the ThO_2 compact, weighted with a 10-gram ThO_2 compact, and the whole assembly placed in an open rhenium crucible.

Diffusion treatments were conducted at 1800°C for 16 hours, 2200°C for 4 hours, and 2400°C for 2 hours in an argon atmosphere. Two treatments were also carried out in a hydrogen atmosphere, one at 2400°C for 2 hours and a second at 2500°C for 3 hours.

The reacted couples were mounted in thermosetting cement and sectional normal to the mating surface at approximately the diameter of the compacts. The exposed surfaces were then ground and polished. The couple treated at 1800°C did not adhere and consequently the exact alignment of the mating surface could not be determined. With this sample, only that portion of the interdiffusion zone adhering to the ThO_2 compact was analyzed.

The concentration gradients for both uranium and thorium were determined by electron microprobe analyses. The specimen was moved slowly under the electron beam and the intensity recorded as a function of distance. (This method is not the most ideal since the short integrated time per unit area is too small to eliminate statistical counting errors.) The tungsten marker technique was not too successful because the large size of tungsten agglomerates did not permit a fine line of demarcation; a satisfactory marking was obtained only on the couple treated at 2500°C . The experimental curves determined on the sample treated at 2500°C are given in Figure 3.4 to illustrate representative concentration profiles for uranium and thorium and also to verify the more rapid diffusion of uranium as shown by the displacement of the tungsten markers toward the UO_2 region.

The Boltzmann-Matano analysis⁴ was used to determine the interdiffusion coefficients, $\tilde{D}$, from the concentration gradient at different values of concentration. In this analysis, provision is made for the variation with concentration of the constant of Fick's diffusion equation. The interdiffusion coefficient at a particular concentration is a composite value for the two diffusing species. $\tilde{D}$ is evaluated by the expression

$$\tilde{D} = -\frac{1}{2t} \frac{dx}{dc} \int_{C_0}^{C_1} xdc$$

The inverse slope dx/dc is measured at each composition and the area $\int_{C_0}^{C_1} xdc$ is measured by graphical integration. The coefficients were calculated from the thorium concentration curve neglecting any corrections for absorption effects and the effects of porosity and grain size. The interdiffusion coefficients are tabulated in Table 3.1. $\tilde{D}$ values at 80 and 20 weight percent thorium are plotted as a function of reciprocal temperature in Figure 3.5.

The precision of the Matano analysis and variations in the concentration profiles introduce considerable uncertainty concerning the dependence of $\tilde{D}$ upon composition and oxygen-to-uranium ratio. Errors at the concentration limits are large because of the small value

⁴P. G. Shewman, *Diffusion in Solids*, McGraw-Hill, 1963, pp. 28-31.

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Fig. 3.4 – Electron microprobe analyses for $\text{UO}_2\text{-ThO}_2$ couple heated at 2500°C for 3 hours

of the area integral. The non-uniform microstructure causes scatter in the concentration profile which, in turn, causes variations in the $\tilde{D}$ values. In general, the interdiffusion coefficients appear to be in approximate agreement with Auskern and Belle's findings⁵ for the self-diffusion of uranium in UO_2 . This agreement might possibly be fortuitous although one might predict that the differences in diffusion behavior of uranium and thorium would not be unduly large. A more refined experimental procedure with ideal materials is required to clarify more thoroughly the diffusion behavior of the $\text{UO}_2\text{-ThO}_2$ system.

TABLE 3.1
INTERDIFFUSION COEFFICIENTS FOR $\text{UO}_2\text{-ThO}_2$

Thorium Content, ^a wt %	Interdiffusion Coefficient, cm^2/sec				
	1800°C (Argon)	2200°C (Argon)	2400°C (Argon)	2400°C (Hydrogen)	2500°C (Hydrogen)
85	8.4×10^{-13}	0.8×10^{-11}	1.8×10^{-11}	2.0×10^{-11}	3.9×10^{-11}
80	6.4×10^{-13}	1.5×10^{-11}	1.4×10^{-11}	2.5×10^{-11}	4.7×10^{-11}
70	9.0×10^{-13}	1.1×10^{-11}	1.7×10^{-11}	1.6×10^{-11}	3.8×10^{-11}
60	1.3×10^{-12}	1.5×10^{-11}	1.8×10^{-11}	0.9×10^{-11}	2.9×10^{-11}
50	1.0×10^{-12}	2.0×10^{-11}	1.5×10^{-11}	1.0×10^{-11}	3.3×10^{-11}
40		2.1×10^{-11}	2.4×10^{-11}	1.2×10^{-11}	4.0×10^{-11}
30		1.9×10^{-11}	2.9×10^{-11}	1.1×10^{-11}	6.0×10^{-11}
20		2.1×10^{-11}	3.5×10^{-11}	1.0×10^{-11}	1.2×10^{-10}
10		1.8×10^{-11}	4.5×10^{-11}	1.4×10^{-11}	1.7×10^{-10}

^aIntercept points on the concentration profiles for thorium.

⁵A. B. Auskern and J. Belle, "Uranium Ion Self Diffusion in UO_2 ," *Journal of Nuclear Materials*, Vol. 3, 1961, pp. 311–319.

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Fig. 3.5—Log of interdiffusion coefficient, $\tilde{D}$, versus reciprocal temperature

COMPATIBILITY OF UO_2 WITH REFRACTORY METALS

During the present report period, detailed evaluation of previously tested metal- UO_2 capsules was carried out. Particular attention was given to Ta-encapsulated $\text{UO}_{2.00}$ tested in dry hydrogen for long periods, resulting in extremely large changes in stoichiometry. Also examined were two Re-encapsulated $\text{UO}_{2.00}$ samples containing internal Ta, tested under thermal gradient conditions, and various Ta-encapsulated UO_2 samples tested under thermal cycle conditions.

In addition to these microstructure studies, two thermal gradient tests of Re-encapsulated W-60 UO_2 (vol %) were carried out.

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Microstructure Evaluations

Isothermal Tests – Four Ta-encapsulated urania specimens, Table 3.2, were tested isothermally. Three of the test capsules contained leaks after testing, and since the stoichiometry changes were very large and approached the U-UO_{2-x} phase boundary, it was of interest to determine whether interaction between the Ta and the urania was responsible for the leaks.

In each of the four capsules tested isothermally, several cracks extended radially from the inner surface of the Ta cladding toward the external surface with a few of the cracks extending all the way through the Ta. Most of the cracks contained free uranium, indicating that they existed in the Ta capsule during cooling. Metallographic examination showed no cracks in the Ta tubing from which the capsules are made.

From 1 to 2 percent Ta was detected in the free uranium in both the urania and the cracks. This may indicate that molten uranium was present in the capsule at test temperature. On the other hand, it is more likely that the U-Ta solid solution began to form when the uranium partial molar free energy in the UO_{2-x} reached the necessary value as the O/U ratio decreased – this condition probably exists short of arriving at the U-UO_{2-x} phase boundary.

Thermal Gradient Tests – Specimen Ta-L-10, Table 3.2, showed stoichiometry changes so great that the resultant composition gradient was at or near the U-UO_{2-x} phase boundary at all temperatures. Free uranium was observed in the urania throughout the length of the capsule; however, more was present at the hot end. The numerous as-sintered small pores were still present in the cool end but had coalesced to large voids at the hot end. Faint, white streaks in the tantalum at the cool end were identified as tantalum carbide. Since Ta discs used as end caps are ground to obtain a good fit with the Ta can before the capsules are sealed by welding, it is possible that in the case of this capsule some carbon contamination remained from the grinding operation.

In addition to this test, metallographic examination was completed on two other thermal gradient capsules. These capsules were tested⁶ to determine whether or not the presence of an oxygen getter material in a capsule containing initially stoichiometric UO_2 would permit the formation of a composition gradient under thermal gradient conditions.

In both capsules, tantalum was used as the gettering material and rhenium was chosen for the external container to prevent any oxygen loss to the environment. In one test, the tantalum was in the form of a 4-gram coil of 0.051-cm-thick arc-cast sheet, total length about 1 cm, placed in the cold end of the rhenium capsule. In the other, a 12-cm-long Ta-encapsulated UO_2 specimen was encased in a rhenium can. Both of the tests were performed in a flowing hydrogen atmosphere for 20 hours; and, as reported previously,⁷ a significant concentration gradient developed. Post-test oxygen contents were 2300 ppm for the Ta insert and an average of 1600 ppm for the Ta can.

Metallographic examination revealed massive tantalum oxide deposits in the grain boundaries of the Ta insert, together with the intersecting straight lines that indicate tantalum oxide (Widmanstätten precipitate) in the cubic planes of the tantalum. X-ray examination of a large Ta grain showing the Widmanstätten lines indicated that the oxide platelets causing the lines were in the 010, 100, and 110 planes of the Ta. At the cool end of the capsule, the location of the Ta insert, a reaction layer was observed on the inner surface of the Re. Since no free uranium was observed in the urania phase in this

⁶"Fifth Annual Report – High-Temperature Materials Programs, Part B," GE-NMPO, GEMP-400B, February 28, 1966, pp. 52–53.

⁷Ibid.

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TABLE 3.2
DATA FOR TANTALUM-ENCAPSULATED URANIA
TESTED IN HYDROGEN

Test No.	Temperature, °C	Time, hr	Oxygen-to-Uranium Ratio	
			Initial	Final
TAAC-105	2150	115	2.003	1.785 ^a
TAAC-104	2350	41	2.003	1.705 ^a
TAAC-107	2350	71	2.003	1.692 ^b
TAAC-111	2350	50	2.003	1.683 ^a
Ta-L-10 ^c	1700 - 2370	120	2.003	- a

^aCapsule leaked after test.

^bCapsule was thermal cycled three times because of furnace failure and broke open before it could be checked for leaks.

^cThermal gradient test, final O/U ratios ranging from 1.942 to 1.795.

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region, it is probable that the reaction occurred between the Re and Ta. Composition of the reaction layer will be determined by electron microprobe analysis.

The capsule consisting of Ta-clad urania overlaid with rhenium was subjected to both metallographic and electron microprobe examination. Small deposits of free uranium were found in the urania grain boundaries in the hot end of the capsule but none in the cool end, confirming that the degree of substoichiometry was greater in the hot end of the capsule. A few minute bright spots in the urania phase were found to contain varying amounts of Fe, Cr, and Ni. Possible sources of this contamination are being investigated. An interaction layer between Ta and Re was observed the entire length of the capsule. Except for a very narrow layer at the cool end, the interaction layer consisted of two regions. One region next to the Re overlaid showed a Re content of approximately 55 to 70 weight percent and DPH hardness of approximately 1800; the other region next to the Ta showed a Re content of approximately 10 to 25 weight percent and a DPH hardness of approximately 600. No free uranium was detected in this phase.

Thermal Cycle Tests - Tests of sealed capsules, fabricated from Ta, Ta - 10W, or Ta overlaid with Re and each containing urania, initial O/U ratio either 2.003 or 1.977, were reported previously.⁸ The capsules were tested in a static helium atmosphere at about 0.1 kg/cm² gage pressure. To reduce or eliminate the small gap between oxide and cladding, some capsules were autoclaved for 1 hour at 1650°C in helium at 703 kg/cm² before thermal cycling. Thermal cycle test conditions are summarized in Table 3.3, and data for the tests are presented in Table 3.4.

All the capsules that had been autoclaved for 1 hour expanded during thermal cycling even though density of the urania pellets within the capsules increased at the same time. The "as-sealed" capsules shrank up to 100 hours of test time at 2150°C, but Ta-clad UO_{2.003} capsules tested for an additional 100 hours at 2150° (30 "C" cycles) began to expand again. These results suggest that mechanisms other than differential thermal expansion were responsible for the volumetric expansion observed. Details of the mechanisms are not known, but the expansion is probably caused by formation of some vapor species within the sealed capsule.

In each furnace run three tantalum coupons were included on which hardness measurements were taken to indicate atmospheric contamination. The hardness of the coupons increased from a DPH value of approximately 100 to approximately 300 as a result of 100 hours at 2150°C with 30 "C" cycles, indicating some contamination present in the

⁸"High-Temperature Materials Program Progress Report No. 52, Part B," GE-NMPO, GEMP-52B, October 20, 1965, pp. 29-30.

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TABLE 3.3
THERMAL CYCLE TEST CONDITIONS

Cycle Code	Total Cycle Time, min	Time to 2150 °C, min	Time at 2150 °C, min	Time to 260 °C, min
A	45	20	5	20
B	90	25	5	60
C	360	40	200	120

TABLE 3.4
DATA FOR THERMAL CYCLE TESTING
OF ENCAPSULATED URANIA

Capsule Material	Test Conditions			O/U Ratio	
	No. of Cycles			Time at 2150 °C, hr	
	A	B	C	Before	After
Ta	—	17	90	301.5	2.003 1.982
Ta ^{a, b}	—	17	90	301.5	2.003 1.986
Ta	—	47	30	104	2.003 1.994
Ta ^a	—	17	30	101.5	1.977 1.995
Ta ^b	—	17	—	1.5	1.977 1.979
Ta — 10W	—	47	30	104	2.003 1.992
Ta — 10W ^b	—	17	—	1.5	2.003 1.996
Ta — 10W ^a	—	17	30	101.5	2.003 1.988
Re/Ta	—	—	30	100	2.003 2.004
Re/Ta ^b	100	—	—	100	2.003 1.999
Re/Ta ^b	—	—	30	100	1.977 1.981

^aNot autoclaved before test.

^bShowed cladding leak after test.

helium. With the exception of the Re-clad capsules discussed below, the average hardness of the tantalum in the capsules increased by roughly the same amount as that of the coupons.

In one capsule containing a UO_{1.977} pellet, metallographic examination after the capsule was autoclaved revealed a metallic phase of high uranium content which formed a continuous layer between the urania and the tantalum. A second phase, approximately 97.0Ta — 1.5U (wt %) with an oxygen content higher than that of the tantalum matrix was present in the cladding at the urania — tantalum interface. Metallic uranium deposits were also present in the grain boundaries of the urania.

Metallographic examination of Ta claddings removed from tested capsules revealed nonmetallic or oxide precipitates, identified as urania by electron microprobe analysis, in the claddings of all but one of the capsules tested. The amount of urania precipitate observed was significantly greater in the cladding of the capsules that contained sub-stoichiometric urania prior to testing. In the case of the one exception, only a very small portion of the cladding was mounted and polished. Figure 3.6 shows photomicrographs of sections from three test capsules.

All the Re-overclad capsules showed urania precipitation in the Ta similar to that observed in the capsules clad with Ta only. Furthermore, as shown in Figure 3.7, an interdiffusion zone was formed at the Ta — Re interface. Boundaries of the zone were diffusion voids in the Ta and a Re-Ta-O layer in the Re. The presence of oxygen at the Ta diffusion front and urania in the Ta showed that both oxygen and uranium had diffused from the urania pellet into the Ta cladding. The Re overcladding served as a

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Interface of Ta-clad urania after 301.5 hours at 2150°C and 107 cycles between 2150° and 260°C. Initial O/U = 2.003, final O/U = 1.986. (Neg. 6533, as-polished, 500X)

Interface of Ta-10W-clad urania after 101.5 hours at 2150°C and 47 cycles between 2150° and 260°C. Initial O/U = 2.003, final O/U = 1.988. (Neg. 5929, as-polished, 100X)

Inner surface of Ta from Ta-clad spiked urania after 1.5 hours at 2150°C and 17 cycles between 2150° and 260°C. Initial O/U = 1.977, final O/U = 1.979. (Neg. 5499, as-polished, 250X)

Fig. 3.6 – Photomicrographs of thermal cycle test capsules

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barrier to further oxygen diffusion and caused the formation of a complex Re-Ta-O layer. Two layers were visible in the metallic portion of the interdiffusion zone. As shown in Figure 3.7, the layer next to the Re was extremely hard (DPH ~1700), and the layer next to the Ta was less hard (DPH ~500).

Fig. 3.7 - Photomicrograph of Re-overclad Ta-clad urania capsule after 100 hours at 2150°C and 30 cycles between 2150° and 260°C. Initial O/U = 1.977, final O/U = 1.981 (Neg. 6530, as-polished, 100X)

The interdiffusion zone observed with the Re-overclad thermal cycle capsules was similar to that observed in the Re-overclad Ta-clad urania thermal gradient capsule tested in hydrogen in that there were two Re-Ta layers, the one next to the Re being extremely hard. The zones were different in that no Re-Ta-O layer or diffusion voids were observed in the thermal gradient capsule.

All Re-overclad thermal cycle capsules had a second-phase metallic layer on the outer surface identified as Re-Ta alloy, and another layer just underneath the Re-Ta alloy identified as Re-Ta-O. All the Re-overclad capsules were thermal cycled in Ta crucibles. Apparently a sufficient oxygen partial pressure existed in the He to permit transfer of Ta from the crucible to the test capsule as a volatile oxide of Ta.

Formations of urania in the Ta cladding of Re-overclad capsules containing pre-test stoichiometric UO_2 was limited to the end caps, with the cylindrical walls of the Ta capsule showing no penetration. The identification of the Re-Ta-O layer at the Re-Ta interface of the leak-tight capsules indicated that the oxygen could have come only from the urania pellet; although post-test ignition analysis of the urania (2.004) and the absence of visible unalloyed uranium precipitates in the urania was in apparent disagreement. A possible explanation is that the tantalum acts as a sink for oxygen which diffuses from the UO_2 at test temperature. This would create a very slight degree of substoichiometry

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TABLE 3.5
ENCAPSULATED W - 60UO₂ TESTED IN A THERMAL GRADIENT

Test No.	Re-D-1 ^a	Re-25-2 ^a
Capsule Material	Rhenium	Rhenium ^b
Time, hr	70	70
Atmosphere	Argon	Argon
Specimen length, cm	11.14	11.36
W-UO ₂ content, g	262.137 ^c	279.432 ^c
Total weight, g	330.024	431.243
Initial O/U ratio	2.000	1.972 ^d
Weight change, g	-0.012	-0.079
Leak	Yes	Yes
	Temperature, °C	Final O/U ratio
	~1760	2.000
	2010	2.000
	2220	2.000
	2370	1.999
	2420	2.000
	2465	1.999
	2485	2.000
	Temperature, °C	Final O/U ratio
	~2000	1.997
	2300	1.993
	2510	1.984
	2660	1.973
	2700	1.967
	2700	1.960
	2700	1.967

^aAutoclave bonded.

^bDouble layer of 0.051-cm-thick wrought sheet.

^c46% UO₂ by weight.

^dCalculated from the amount of metallic uranium determined by the hydriding method. Precision about ± 0.003 ; absolute accuracy dependent on distribution of the metallic precipitate.

in the UO₂ and lead to some uranium precipitation during cooling. The latter could then enter the tantalum and be reconverted to UO₂ during subsequent cycles. White metallic inclusions, identified as metallic Ta, were observed in the urania from Re-overclad capsules regardless of whether the urania was stoichiometric or substoichiometric before test. Free uranium was still present after test in the initially substoichiometric urania.

In thermal cycle testing of stoichiometric or substoichiometric urania encapsulated in Ta or Ta - 10W in static helium atmospheres from 2150° to 260°C, oxygen loss or gain through the cladding occurs as the urania equilibrates with the atmosphere. In this study, the equilibrium O/U ratio determined by ignition analysis may be slightly⁹ negatively biased by the presence of metallic inclusions, other than U, in the urania. However, on the basis of results obtained with capsules subjected to 107 cycles and with 300 hours accumulated test time at 2150°C, a limiting O/U ratio of 1.985 is indicated. This value is in good agreement with that reported previously¹⁰ for isothermal testing of Ta-encapsulated urania in argon at 2150°C.

Thermal Gradient Tests

In the previous report,¹¹ several tests were discussed in which Re-encapsulated W-UO₂ specimens were heated in a thermal gradient (temperature range from about 1500° to 2500°C). Although the specimens were autoclave bonded before test, separation over

⁹The amount of contamination is not expected to be significant. A contamination, for example, of 0.1% Ta in UO_{1.985} would affect the O/U ratio by only 0.003 units.

¹⁰"Fourth Annual Report - High-Temperature Materials and Reactor Component Development Programs, Volume II - Materials," GE-NMPO, GEMP-334B, February 26, 1965, p. 36.

¹¹"Fifth Annual Report - High-Temperature Materials Programs, Part B," GE-NMPO, GEMP-400B, February 28, 1966, pp. 50-52.

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most of the cladding - core interface developed as a result of formation of brittle W-Re alloys. Two tests were conducted in hydrogen and one in argon. In all three, the UO_2 was initially substoichiometric and a concentration gradient developed which corresponds to an enthalpy of about 35 kcal.

A fourth such test was completed (Re-25-2: Table 3.5) with a specimen in which the initial composition was $\text{UO}_{1.972}$. This test, for 70 hours in argon, is essentially a repeat of a previous test except that it was tested to a higher temperature (2700°C). Although the results are somewhat scattered, the concentration gradient is in qualitative agreement with the enthalpy of 35 kcal observed previously.

As discussed previously,¹¹ these results suggest that tungsten at the lower temperatures may be acting as an oxygen sink, thus accentuating the composition gradient which would form in 100 percent UO_2 . The possibility of creating a composition gradient in initially stoichiometric UO_2 in the presence of an oxygen sink was demonstrated for Re-encapsulated $\text{UO}_{2.00}$ containing tantalum inside the capsule.¹¹ To determine whether stoichiometric UO_2 would behave similarly in the presence of tungsten, test Re-D-1 was performed. The capsule was fabricated exactly as those above except that the cores, prior to assembly, were given a post-sinter treatment in wet hydrogen (0°C dewpoint) at 1400°C for 18 hours followed by dry hydrogen at 1200°C for 18 hours. Analysis of this starting material by the hydriding method showed less than 0.005 percent free uranium, which corresponds to a composition of UO_{2-x} , with $x < 0.0003$.

The test was performed in argon for 70 hours with a temperature gradient from about 1760° to 2485°C . The good bond which existed prior to test was largely ruptured. A leak was found after test, but since the weight loss of the capsule was small, no significant amount of oxygen loss from the UO_2 is believed to have occurred. Results are given in Table 3.5. The slight evidence of substoichiometry is not considered significant since the variation in O/U ratio is less than the nominal ± 0.003 units assigned as the precision of the hydriding method. Similar tests of longer duration are needed to determine whether the present results represent equilibrium. Also, microstructures must be studied to determine, at least qualitatively, whether the hydriding method is measuring the total amount of free uranium present in these specimens.

The apparent lack of formation of a composition gradient in this test may indicate that the starting material was slightly hyperstoichiometric, which would not be detected by the hydriding method used for analysis. Similar tests will be performed starting with core material for which the post sinter treatment is limited to dry hydrogen.

WORK PLANNED FOR NEXT PERIOD

Thermal gradient studies will be continued to obtain further information about the degree and rate of formation of a composition gradient in stoichiometric UO_2 when an oxygen getter is present.

Vapor pressure measurements of UO_{2-x} will be completed. The thermobalance will be used in studies of non-equilibrium systems such as kinetics of composition change of UO_2 under free vaporization conditions and also when enclosed in metal capsules.

Interdiffusion of UO_2 and ThO_2 will be studied further with particular emphasis on time as a variable. Specimens of higher density will be used to minimize possible effects of porosity on the measurements.

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4. HIGH-TEMPERATURE RESEARCH ON CARBIDES FOR FUEL AND STRUCTURAL APPLICATIONS

(57073)

The objective of this program is to determine the high-temperature physico-chemical properties of refractory carbides for reactor fuel and structural applications.

EQUILIBRIUM STUDIES

Experiments were continued to determine the solid TaC_x compositions in equilibrium with hydrogen atmospheres whose carbon activities were calculated from their measured hydrocarbon contents. Emphasis was placed on attempts to establish equilibrium compositions in the range between $TaC_{0.8}$ and $TaC_{0.9}$ at $2150^\circ C$. Most compositions reported previously¹ were in the range from $TaC_{0.9}$ to $TaC_{0.99}$. To achieve the lower solid composition range, a series of tests was initiated in which the estimated carbon concentration in the gaseous atmosphere varied from about 5 ppm at $1800^\circ C$ to about 30 ppm at $2150^\circ C$. In contrast to the earlier results, difficulties were encountered in achieving equilibrium for samples simultaneously approaching an intermediate equilibrium composition from both higher and lower C/Ta ratios. The effect was particularly pronounced under conditions of low carbon activity; i. e., gas compositions containing less than 10 ppm total carbon. The problem encountered was a slow apparent decrease in C/Ta ratio of the solid with time after apparently reaching an equilibrium value. The effect is demonstrated in Figure 4.1 which shows composition calculated from lattice parameter as a function of time at $2150^\circ C$ for one sample from this series of experiments, and the hydrocarbon content of the hydrogen after each run. Note the "tailing-off" of lattice parameters after 18 hours at temperature and the "hump" in the curve for the sample which had the initial composition of $TaC_{0.80}$. This decrease in unit cell size may be attributable to one or more of the following possible causes:

1. Contamination of the sample by metallic elements from the furnace fixtures
2. Oxidation of the samples due to trace quantities of oxygen or water vapor contamination of the test atmosphere
3. Decrease in carbon activity in the test atmosphere.

Chemical analyses of several typical samples of TaC_x were performed for W, Re, and Mo to determine whether significant contamination by these metals occurred during the tests. Analyses showed the following levels for each element for the experimental samples and the starting powders:

Element	Starting Material, ppm	After 16 hr at $2170^\circ C$, ppm	After 13 hr at $2300^\circ C$, ppm
Re	12	548	1340
Mo	< 3	7	8
W	< 3	19	4

¹"Fifth Annual Report - High-Temperature Materials Programs, Part B," GE-NMPO, GEMP-400B, February 28, 1966, p. 141.

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These data show that Re is the major contaminant and the content of this impurity increases as the temperature increases. Since the vapor pressure of Re at these temperatures is about 10^{-9} atmospheres, Re is transferred by a solid-state diffusion process from the Re sample holder. However, on the basis of relative atomic radii of Ta and Re, the 1340 ppm of Re observed in the sample heated at 2300°C would decrease the composition estimated from lattice parameters by only 0.002 in apparent C/Ta ratio. The other impurities would have no measurable effect. Consequently, on the basis of these observations, the drift in composition cannot be attributed to contamination by the refractory-metal elements.

Fig. 4.1—Composition as a function of time for $\text{TaC}_{0.993}$ and $\text{TaC}_{0.800}$ heated in $\text{H}_2 + \text{CH}_4$ at 2150°C

Experiments were initiated to determine if water vapor in the test atmosphere² contributes to the difficulty of estimating composition from X-ray lattice parameters (because of possible formation of $\text{Ta}(\text{C}_x\text{O}_y)$ with lower lattice parameter than TaC_x). Several runs were made at 2150°C in which the hydrogen gas was passed through a copper coil submerged in a liquid nitrogen bath. The furnace outlet gas was monitored for water vapor continuously throughout the tests. The "tailing-off" effect shown in Figure 4.1 was observed in each sample of this series. The water vapor content was 0.2 to 0.4 ppm throughout each test in contrast to the 3 to 10 ppm estimated to be present in the earlier runs. During the series of tests, the carbon activity decreased from 9.9 ppm to 4.2 ppm CH_4 . There is no evidence of a sudden increase in oxygen or water vapor pressure during the test. Furthermore, since the drift was observed in samples heated in dried H_2 (< 1 ppm H_2O), it is concluded that the "tailing-off" or drift in composition with time is associated primarily with the decrease in carbon activity in the atmosphere.

Because of the decrease in carbon activity of the atmosphere from run to run, the method of estimating equilibrium composition was changed. Previously, the equilibrium compositions were calculated from X-ray lattice parameters by fitting a pair of exponential curves to a_{O} values for two TaC_x samples approaching equilibrium from opposite sides.

²Although water vapor at room temperature is converted largely to CO at test temperature, it will be referred to as water vapor in this report.

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However, this method requires that the gas composition be constant for all runs in a series. A new method of calculating equilibrium composition was introduced. This method assumes merely that the gas composition is constant within a single run. Gas samples taken at the beginning and the end of a test run supported this assumption. The lattice parameters of the two samples before and after a run are fitted by two exponential curves of the form $a = a_{\infty} + be^{-kt}$ which extrapolate to the same equilibrium parameter (a_{∞}), and have the same rate constant (k). Letting h_0 and h_1 be the initial and final lattice parameters of the higher carbon sample, and ℓ_0 and ℓ_1 the corresponding values for the lower carbon sample, the equilibrium parameter at infinite time is given by

$$a_{\infty} = (h_0\ell_1 - \ell_0h_1)/(h_0 + \ell_1 - \ell_0 - h_1)$$

The composition is then estimated by the equation of Bowman.³

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EFFECT OF WATER VAPOR ON DETERMINATION OF THERMODYNAMIC PROPERTIES

To assess the effect of water vapor on the properties of TaC_x determined by the solid – gas equilibrium experiments, a series of tests was run at 2150°C in dried and undried H_2 . Table 4.1 summarizes results, comparing the experimental results for the tests at 2150°C run in undried H_2 (~10 ppm H_2O) with those run in H_2 passed through a liquid N_2 cold trap (0.2 ppm H_2O). Variation in carbon activity due to the presence of oxygen in the test atmosphere cannot account for these results. The presence of oxygen tends to lower the carbon activity, resulting in a more negative value for $RT \ln \left(a_c \frac{1-x}{x} \right)$. The observed effect is in the opposite direction. However, oxidation of TaC_x produces a decrease in lattice parameter leading to an error in the estimation of composition which results in too low an estimate of C/Ta ratio. An error in composition results in a less negative value for $RT \ln \left(a_c \frac{1-x}{x} \right)$ relative to the unoxidized TaC_x , which is the observed effect. Thus,

TABLE 4.1
EFFECT OF TRACES OF WATER VAPOR IN A $H_2 + CH_4$ ATMOSPHERE
ON THE FUNCTION $RT \ln \left(a_c \frac{1-x}{x} \right)$ FOR TESTS AT 2150°C

Solid Compositions ^a (C/Ta)	Atmosphere	Carbon Content, ppm	Activity (a_c)	$RT \ln \left(a_c \frac{1-x}{x} \right)$
0.845	Dried H_2^b	3.5	0.0087	-31.0
0.823	Dried H_2	2.8	0.0074	-31.0
0.817	Dried H_2	4.2	0.0099	-29.4
0.814	Dried H_2	4.2	0.0099	-29.3
				avg. -30.18 ± 0.96
0.880	Undried H_2^c	26.8	0.0335	-25.9
0.859	Undried H_2	27.4	0.0339	-25.0
0.870	Undried H_2	27.4	0.0339	-25.4
0.862	Undried H_2	26.8	0.0335	-25.1
0.805	Undried H_2	8.8	0.0166	-26.6
				avg. -25.60 ± 0.66

^aAs estimated from X-ray analysis.

^bContaining 0.2 ppm H_2O .

^cContaining >10 ppm H_2O .

³A. L. Bowman, "The Variation of Lattice Parameter with Carbon Content of Tantalum Carbide," *Journal of Physical Chemistry*, Vol. 65, 1961, pp. 1596–1598.

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these data show a difference of about 20 percent between values of the function $RT \ln \left(a_c \frac{1-x}{x} \right)$ for the samples heated in dried H_2 and those heated in undried H_2 , due primarily to error in estimating the solid composition. The effect of water vapor traces would be expected to be particularly acute when working at low carbon activities; i. e., when the H_2O vapor content approaches that of the carbon. Therefore, experiments at low carbon activity ($a_c < 0.01$) were conducted in dried H_2 with the water vapor reduced to <1 ppm by passage through a liquid nitrogen trap. These experiments were conducted at 2150° and $1800^\circ C$. The results are summarized in Table 4.2 together with data previously accumulated.⁴ These data were analyzed by multiple regression methods and the following expression obtained:

$$RT \ln \left(a_c \frac{1-x}{x} \right) = -50.6 + (36.6 \pm 4.7) x - (4.4 \pm 1.1) 10^{-3} T$$

where $x = \frac{C}{Ta}$ and T is in degrees Kelvin.

Activity as a function of composition for TaC_x and temperature is plotted in Figure 4.2 for the data summarized in Table 4.2. Tentative isotherms through the data points are indicated in the plot. Further measurements in the carbon activity ranges from 0.1 to 1.0 and for 0.001 to 0.01 are planned.

TABLE 4.2

CARBON ACTIVITY AND EXPERIMENTAL VALUES OF $RT \ln \left(a_c \frac{1-x}{x} \right)$
FOR SOLID - GAS EQUILIBRIUM COMPOSITIONS AT
VARIOUS TEMPERATURES

Temperature, °C	Estimated Equilibrium, C/Ta ratio	Carbon In Atmosphere As CH_4 , ppm	Carbon Activity (a_c)	$RT \ln \left(a_c \frac{1-x}{x} \right)$
1800	0.805	0.6	0.0014	-32.8
1800	0.926	12	0.0247	-25.7
1800	0.931	14	0.0283	-25.4
1800	0.925	12	0.0147	-25.6
1800	0.936	14	0.0283	-25.7
1830	0.927	22	0.0418	-23.9
2035	0.928	16	0.0287	-28.0
2035	0.933	32	0.0450	-26.3
2150	0.845	3.5	0.0085	-31.0
2150	0.823	2.8	0.0073	-31.0
2218	0.914	34	0.0342	-28.4
2218	0.924	55	0.0449	-27.5
2250	0.995	Saturated	1	-26.5
2257	0.897	51	0.0401	-27.1
2300	0.872	15	0.0185	-30.2
2300	0.875	21	0.0225	-29.3
2300	0.869	21	0.0225	-29.1
2300	0.866	15	0.0185	-30.0
2300	0.994	Saturated	1	-26.3
2344	0.900	38	0.0292	-29.8
2344	0.994	Saturated	1	-26.6
				avg. -27.9

⁴"Fifth Annual Report - High-Temperature Materials Programs, Part B," GE-NMPO, GEMP-400B, February 28, 1966, pp. 149-155.

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Fig. 4.2 – Carbon activity as a function of composition of TaC_x at various temperatures (°C)

WORK PLANNED FOR NEXT PERIOD

Continued effort will be devoted to determining the estimated compositions (i. e., C/Ta ratios) in dry H_2 (<1.0 ppm H_2O) and to re-evaluate previous data in light of these experiments. The experiments will cover the homogeneity range for TaC from $TaC_{0.7}$ to $TaC_{0.99}$, with emphasis on carbon activity in the ranges between 0.001 to 0.01 and 0.1 to 1.0.

The solid – gas equilibrium technique will be extended to determine activity versus composition for UC using the rhenium-encapsulation process.

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5. APPENDIX

The "High-Temperature Materials Program Progress Reports" previously issued in this series are listed below. The first two reports were each issued as one document, containing both the classified and unclassified portions. The subsequent reports were issued as two documents; part A, the unclassified portion and part B, the classified portion.

<u>Report No.</u>	<u>Report Period</u>	<u>Publication Date</u>
GEMP-1	May 1961 - June 30, 1961	July 15, 1961
GEMP-2	July 1, 1961 - July 31, 1961	August 15, 1961
GEMP-3, A and B	July 1, 1961 - August 31, 1961	September 15, 1961
GEMP-4, A and B	August 1, 1961 - September 30, 1961	October 15, 1961
GEMP-5, A and B	August 15, 1961 - October 15, 1961	November 15, 1961
GEMP-6, A and B	September 15, 1961 - November 15, 1961	December 15, 1961
GEMP-7, A and B	October 15, 1961 - December 15, 1961	January 15, 1962
GEMP-106, A and B (First Annual Report)	Calendar Year 1961	February 28, 1962
GEMP-9, A and B	January 1, 1962 - February 15, 1962	March 30, 1962
GEMP-10, A and B	January 1, 1962 - March 15, 1962	April 16, 1962
GEMP-11, A and B	February 15, 1962 - April 15, 1962	May 15, 1962
GEMP-12, A and B	March 15, 1962 - May 15, 1962	June 15, 1962
GEMP-13, A and B	April 15, 1962 - June 15, 1962	July 31, 1962
GEMP-14, A and B	May 15, 1962 - July 15, 1962	August 15, 1962
GEMP-15, A and B	June 15, 1962 - August 15, 1962	September 15, 1962
GEMP-16, A and B	July 15, 1962 - September 15, 1962	October 15, 1962
GEMP-17, A and B	August 15, 1962 - October 15, 1962	November 15, 1962
GEMP-18, A and B	September 15, 1962 - November 15, 1962	December 14, 1962
GEMP-19, A and B	October 15, 1962 - December 15, 1962	January 25, 1963
GEMP-177, A and B (Second Annual Report)	Calendar Year 1962	February 28, 1963
GEMP-21, A and B	January 1, 1963 - February 15, 1963	April 23, 1963
GEMP-22, A and B	January 1, 1963 - March 15, 1963	April 30, 1963
GEMP-23, A and B	February 15, 1963 - April 15, 1963	May 31, 1963
GEMP-24, A and B	March 15, 1963 - May 15, 1963	June 28, 1963
GEMP-25, A and B	April 15, 1963 - June 15, 1963	July 31, 1963
GEMP-26, A and B	May 15, 1963 - July 15, 1963	August 16, 1963
GEMP-27, A and B	June 15, 1963 - August 15, 1963	September 30, 1963
GEMP-28, A and B	July 15, 1963 - September 15, 1963	November 11, 1963
GEMP-29, A and B	August 15, 1963 - October 15, 1963	November 29, 1963
GEMP-30, A and B	September 15, 1963 - November 15, 1963	December 31, 1963
GEMP-31, A and B	October 15, 1963 - December 15, 1963	January 24, 1964
GEMP-270, A and B (Third Annual Report)	January 1, 1963 - January 31, 1964	February 28, 1964

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<u>Report No.</u>	<u>Report Period</u>	<u>Publication Date</u>
GEMP-34, A and B	February 1, 1964 - March 15, 1964	April 15, 1964
GEMP-35, A and B	February 1, 1964 - April 15, 1964	May 28, 1964
GEMP-36, A and B	March 15, 1964 - May 15, 1964	June 19, 1964
GEMP-37, A and B	April 15, 1964 - June 15, 1964	July 31, 1964
GEMP-38, A and B	May 15, 1964 - July 15, 1964	August 19, 1964
GEMP-39, A and B	June 15, 1964 - August 15, 1964	September 30, 1964
GEMP-40, A and B	July 15, 1964 - September 15, 1964	October 15, 1964
GEMP-41, A and B	August 15, 1964 - October 15, 1964	November 30, 1964
GEMP-42, A and B	September 15, 1964 - November 15, 1964	December 18, 1964
GEMP-43, A and B	October 15, 1964 - December 15, 1964	January 29, 1965
GEMP-334, A and B (Fourth Annual Report)	January 31, 1964 - January 31, 1965	February 26, 1965
GEMP-46, A and B	February 1, 1965 - March 15, 1965	April 15, 1965
GEMP-47, A and B	February 1, 1965 - April 15, 1965	May 28, 1965
GEMP-48, A and B	March 15, 1965 - May 15, 1965	June 25, 1965
GEMP-49, A and B	April 15, 1965 - June 15, 1965	July 28, 1965
GEMP-50, A and B	May 15, 1965 - July 15, 1965	August 20, 1965
GEMP-51, A and B	June 15, 1965 - August 15, 1965	September 30, 1965
GEMP-52, A and B	July 15, 1965 - September 15, 1965	October 20, 1965
GEMP-53, A and B	August 15, 1965 - October 15, 1965	November 1965
GEMP-54, A and B	September 15, 1965 - November 15, 1965	December 20, 1965
GEMP-55, A and B	October 15, 1965 - December 15, 1965	January 21, 1966
GEMP-400, A and B (Fifth Annual Report)	January 31, 1965 - January 31, 1966	February 28, 1966

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