204
11-24 c

MLM-1706

DT-1634

MLM-1706

MASTER

***The Compatibility of $^{238}\text{PuO}_2$
with Various Refractory
Metals and Alloys:
Interim Report***

J. E. Selle, J. J. English, P. E. Teaney,

and J. R. McDougal

THIS DOCUMENT CONFIRMED AS
UNCLASSIFIED
DIVISION OF CLASSIFICATION
BY JH Kahn/amb
DATE 12/1/70

AEC Research and Development Report

MOUND LABORATORY

operated by

MONSANTO RESEARCH CORPORATION

a subsidiary of Monsanto Company
for the

U. S. ATOMIC ENERGY COMMISSION

Monsanto

PRINTED IN THE UNITED STATES OF AMERICA

Available from

Clearinghouse for Federal Scientific and Technical Information
National Bureau of Standards, U.S. Department of Commerce
Springfield, Virginia 22151

Price: Printed Copy \$3.00; Microfiche \$0.65

LEGAL NOTICE

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

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

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

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

DISCLAIMER

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

DISCLAIMER

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

The Compatibility of $^{238}\text{PuO}_2$ with Various Refractory Metals and Alloys: Interim Report

J. E. Selle, J. J. English, P. E. Teaney, and J. R. McDougal

Issued: October 23, 1970

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

MONSANTO RESEARCH CORPORATION

A Subsidiary of Monsanto Company

MOUND LABORATORY

Miamisburg, Ohio 45342

operated for

UNITED STATES ATOMIC ENERGY COMMISSION

U.S. Government Contract No. AT-33-1-GEN-53

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	5
INTRODUCTION	6
PROCEDURE	7
PHYSICAL PROPERTY AND THERMODYNAMIC CONSIDERATIONS	10
TANTALUM	12
1000°C	12
1200°C	13
1500°C	14
1700°C	15
Discussion	16
TANTALUM-10 WT % TUNGSTEN	17
1000°C	19
1200°C	19
Variable Impurity Studies at 1200°C	20
1500°C	21
1700°C	21
2500°C	22
Discussion	22
T-111 (222) ALLOY	23
T-222 at 1000°C	23
T-222 at 1200°C	23
T-111 at 1500°C	24
T-111 at 1700°C	24
Discussion	25
NIOBIUM	26
1500°C	26
1700°C	27
Discussion	27

TABLE OF CONTENTS (CON'T)

	<u>Page</u>
MOLYBDENUM	27
1200°C	27
1500°C	28
1700°C	29
1900°C	29
Discussion	30
TZM ALLOY	31
1200°C	31
1500°C	32
1700°C	32
Discussion	33
MOLYBDENUM-50 WT % RHENIUM AT 1200°C	33
RHENIUM	34
TUNGSTEN	35
1000°C	35
1200°C	35
1500°C	36
Discussion	38
TUNGSTEN-26 WT % RHENIUM	38
1000°C	38
1200°C	38
1500°C	39
Discussion	39
HAFNIUM	40
ZIRCONIUM	40
GENERAL DISCUSSION	41
Applications and Implications of the Data	43
CONCLUSIONS	44
ACKNOWLEDGEMENTS	46
REFERENCES	47

TABLE OF CONTENTS (CON'T)

	<u>Page</u>
FIGURES	49
TABLES	185
APPENDIXES	197

ABSTRACT

Data accumulated to date on the compatibility of production grade $^{238}\text{PuO}_2$ with various refractory metals and alloys are presented and discussed. The materials discussed are tantalum, tantalum-10 wt % tungsten, T-111, T-222, niobium, molybdenum, TZM, molybdenum-50 wt % rhenium, rhenium, tungsten, tungsten-26 wt % rhenium, hafnium, and zirconium. Test temperatures ranged from 1000 to 2500°C for time periods up to 532 days at the lower temperatures and up to 2000 hr at the higher temperatures. Consequences of the data obtained to date and future work are discussed.

INTRODUCTION

As part of a general research and development project in support of the Radioisotopic Heat Source Program, a study of $^{238}\text{PuO}_2$ with various refractory metals and alloys was initiated. Production grade fuel, produced in accordance with the SNAP-27 specifications, was used in this program. According to these specifications the fuel may contain up to 2.0% of nonactinide cation impurities. Fuel produced to these specifications was used for several reasons. The most important of these is that it is desirable to know what reactions, if any, would take place in an actual heat source capsule in service. At the time these tests were initiated the reference fuel form was PuO_2 microspheres produced according to the SNAP-27 specifications. Secondly, production grade fuel is much more readily available than special purity fuel. In view of the large amounts of fuel needed for the entire program, this is an important consideration.

The intent of the effort is to determine the rates of reactions, if any, mechanisms of the reactions, and the possible effects of these reactions on the integrity of the liner material. A second purpose of this effort is to attempt to identify potential problem areas resulting from the use of this fuel, focus attention upon these areas, and propose solutions to these problems. The philosophy behind selection of materials to be tested was that commercially available refractory metals and alloys would be tested as well as each of the alloying elements.

In view of the extent of this effort, both in terms of the number of materials and the large temperature range of the tests, as well as programmatic needs, it was decided that a thorough review of the data accumulated to date would be desirable. Upon completion of the program a final report will be written. A similar interim report for platinum and platinum-rhodium alloys has been prepared¹, and a report on superalloys will be written in the near future.

Much of the data presented in this interim report has been presented in various Mound Laboratory quarterly reports as well as two summary reports. However, the nature of these reports can result in some confusion because of lack of continuity. Since they are progress reports, they are somewhat incomplete and therefore do not present the entire picture. Therefore, these data will also be included in this report so that all the data can be placed in perspective. Since this is an interim report, some of the data are necessarily incomplete. Not all of the metallography

has been completed on samples that have been removed from the furnace. Many of the samples that have undergone metallography have not been run on the microhardness tester. In addition, most of the x-ray analyses of the fuel after testing have not been completed. These gaps in the data have been the result of time and personnel limitations and the fact that certain program requirements of various design agencies forced concentration of effort on the acquisition of data for particular materials. This concentration of effort on particular materials was conducted at the expense of others.

Since this is an interim report and the data are sometimes incomplete, some of the conclusions reached in this report may no longer be valid at the end of the program. Accumulation of more data may shed more light on the actual mechanisms, and the data and conclusions should be reviewed in this light. Time constraints have prevented a complete literature search on all of the materials discussed in this report. As the program proceeds this deficiency should be eliminated and many of the observations made in the course of this project correlated with prior work on these alloys.

It is the intent of this report to present as much of the data generated as possible. In this way the reader may analyze the data and reach his own conclusions, which may or may not agree with those presented in this report. Not all of the photomicrographs and electron microprobe data obtained are presented in this report. To do so would probably cause more confusion than it would resolve. However, a serious attempt has been made to present as much information as possible without being too redundant.

PROCEDURE

Data were obtained at 1000, 1200, 1500, 1700, and 1900°C. One test was run at 2500°C with tantalum-10 wt % tungsten. In addition, future tests will be run at 2100°C. The total matrix for the refractory metal program is shown in Appendix A. All of the capsules in a given series of tests and the fuel used in a given series of tests were from the same lot of material. The chemical analyses of the capsule materials and fuel referred to in Appendix A are given in Appendixes B and C respectively. Capsule designs used in each case are indicated and are summarized in Appendix D. Some of these capsule designs leave something to be desired. Their design was motivated primarily by a desire to obtain the maximum amount of test data in the shortest period of time for the lowest cost. This meant starting many of the tests with materials already on hand or using an easily obtainable mill product. In some cases the cost of proper tubing was extremely high or delivery time extremely long which necessitated the use of discs of one material embedded in the fuel which, in turn, was contained in a different liner material. A design of this type often leads to complications. This point was discussed in the interim report on platinum and platinum alloys¹ and will be demonstrated in this report as well. The effects of the interrelations between the liner and embedded discs are not always obvious, nor are they always understood.

In all cases, a two layer system was employed. The inner liner containing the fuel was first TIG welded closed. This liner was then decontaminated and welded inside a secondary capsule. With the exception of the 1000°C tests which were TIG welded, the secondary capsules were electron beam welded. In the 1000 and 1200°C tests the outer containers were Hastelloy X, whereas at 1500°C and above the containers were tantalum-10 wt % tungsten. In all of the 1200°C tests a tungsten spacer was placed between the inner liner and the Hastelloy X outer capsule to prevent any interaction between the two materials. This is particularly necessary with tantalum alloys, because a eutectic exists in the tantalum-chromium-nickel system with a melting point of 1165°C.³ All TIG welds on the inner liners were made in an argon atmosphere using high purity argon as a cover gas.

Annealing at 1000 and 1200°C was done in muffle furnaces in an air atmosphere. Oxidation resistance was provided by the Hastelloy X outer container. Hastelloy X begins to melt at 1260°C so that at 1200°C the operating temperature is very close to the maximum useful limit of the outer container. Above 1200°C the oxidation resistance and the creep resistance of Hastelloy X decrease rapidly with temperature. In view of the small margin for error in the operating temperature and the lack of completely fail-safe controllers, the actual operating temperature tended to be on the conservative side. Therefore, the 1200°C temperature of this report should actually be considered as 1150-1200°C. At 1500°C and above, all tests were conducted in a Brew furnace under a vacuum of less than 5×10^{-5} torr.

Metallographic sample preparation was done in a glovebox facility under a nitrogen atmosphere. Sectioning was done with an abrasive cutoff wheel employing 90 grit silicon carbide. The specimens were mounted in a copper-filled diallyl phthalate to provide a conductive mount for electron microprobe analysis.

Coarse grinding of the metallographic mount was done with 180-320 grit silicon carbide paper, and final grinding was done with 600 grit silicon carbide. Carbon tetrachloride was used as a lubricant in grinding and polishing. Rough polishing was done on Texmet* paper with 6 μ m diamond paste with olive oil as a lubricant. An intermediate step of 3 μ m diamond paste on Texmet paper was used. Final polishing was done on microcloth on a vibratory polisher with 0.3 μ m alumina and water as a lubricant. Samples were usually examined in the unetched condition. This is particularly true of samples prepared for electron microprobe analyses, because etching can sometimes selectively leach out certain elements. A summary of the etchants used, when necessary or desirable, is given in Appendix E.

*Texmet is a napless polishing paper supplied by A. B. Buehler, Ltd.

Except for the 1000°C tests, all photomicrographs were taken with a Leitz MM5 metallograph. Photomicrographs for the 1000°C tests were taken with a B & L bench-type metallograph. Microhardness measurements were made with a Leitz miniload hardness tester or with a Leitz microhardness attachment for the MM5 metallograph.

Electron microprobe analysis was done on an Applied Research Laboratories instrument. Two types of analyses were done. In the first type, the electron beam scanning unit of the instrument was used to scan the specimen, and photographs were taken of the distribution of various elements using the signal from the characteristic x-ray to modulate the beam of the cathode ray tube. In this mode of operation the beam is scanned across an area of the sample so that a distribution of that particular element can be obtained. Also, by this technique, photomicrographs were taken with the backscattered electrons from the sample. The photomicrographs obtained in this manner yield a density distribution across the area scanned.

The second type of analysis was done using a finely focused static beam to indicate compositional changes as the specimen was moved under the beam. Analysis was made by driving the stage translation over a selected part of the specimen and feeding the signal from the characteristic x-ray through a rate meter to a strip chart. The resulting trace gives a rough quantitative description for each of the elements sought as a function of the distance across the face of the sample. The data in this report are presented in the form of traces of these strip chart plots superimposed upon each other. The relative vertical displacement of each curve with respect to the others should not be considered as a quantitative comparison of the amount of one element with another. This relative displacement is a function of the counting rate and, hence, is a variable. However, for a given element, the changes in displacement of the curve, excluding electronic noise, can be used to indicate changes in composition. The number adjacent to the identification of each curve is the counting rate used for that particular element. Different counting rates were used in an attempt to obtain maximum sensitivity and still keep the trace on scale. The higher the counting rate for a given percent of scale, of one element with respect to another, the greater is the actual relative amount of that element with respect to the other. At the same time, decreasing the counting rate necessitates an increase in amplification, resulting in an increase in the noise to signal ratio. In order to obtain a more accurate comparison of one element with respect to another, the curves must be normalized with respect to one of the elements. If element B is to be compared with element A the following relationship is used:

$$\frac{\text{Counting rate B}}{\text{Counting rate A}} \times \frac{\% \text{ of scale of element B}}{\% \text{ of scale of element A}} = \text{relative amount of B (1) with respect to A}$$

It should be emphasized that this equation will give only a relative amount of B compared to A. No quantitative comparisons are implied. A further clarification of this point may be obtained from Figure 1, which

shows the relative displacements of tungsten at three different counting rates for a tantalum-10 wt % tungsten alloy. The relative displacement equivalent to 10 wt % tungsten in this alloy is plotted for each of the three counting rates. The counting rate (10^5 , 5×10^5 , 10^6) merely indicates the counting rate, in counts/minute, that will produce the given displacement. In effect, the lower the counting rate the greater is the displacement for a given amount of the element under consideration. The background displacement must also be considered. This background is the zero wt % reading and is caused primarily by the continuous x-ray spectrum of all the elements being excited by the electron beam. In order to make the comparison quantitative, other corrections must be made to compensate for differences in wavelength, peak intensities, absorption, density, etc. At the same time a standard of known composition must be used for comparison. In some cases, when built-in standards were available, attempts were made to obtain more accurate analyses. Even in these cases, however, errors as high as several percent are present because the second and third order corrections were not made.

Several techniques were used to measure the depth of penetration of various elements into the test samples, and any property changes at the reaction interface. These are electron microprobe data, etching and metallographic analysis, and microhardness measurements. The most definitive information is given by the electron microprobe. However, analysis of every sample by the electron microprobe places an inordinate load on this instrument and would result in a considerable delay in the overall program. Therefore, steps are being taken to use metallographic techniques and microhardness measurements as much as possible. In some materials it has not been possible to establish an adequate correlation between microprobe data and one of the other techniques. In these cases the microprobe was then relied upon exclusively. These cases will be discussed at the appropriate place.

In addition to these tests, an attempt was made to determine the lattice parameters of the fuel after each test to determine whether any changes in stoichiometry or structure occurred as a result of the tests. Samples of the fuel powder were loaded into quartz capillaries with an inside diameter of 0.3 mm and a wall thickness of 0.02-0.03 mm. A standard Debye-Scherrer powder camera was used. Filtered copper $K\alpha$ radiation from a high intensity GE x-ray tube was used with exposure times of 2-4 hr. The film was covered with aluminum foil in order to minimize the effects of secondary radiation.

PHYSICAL PROPERTY AND THERMODYNAMIC CONSIDERATIONS

A recent paper³ discussed the importance of knowing the thermodynamics, structure, and vaporization of metal oxides in order to understand high temperature metal/oxide reactions. In this paper it was stated that high temperature reactions can be frequently quantitatively analyzed by assuming that at interfaces, metal/oxide or oxide/gas, thermodynamic equilibrium applies. Within these solids and at interfaces, the rates or processes are diffusion controlled. In addition, oxide vapor

pressures and composition of the vapor species are also important at these elevated temperatures.

Continued efforts are being made in this program to relate the observed high temperature compatibility of the metal container/plutonium dioxide systems with known high temperature properties of metals and oxides. Such high temperature property data are limited, and the systems being investigated are complex. Unfortunately, such complications as 1) the departure of plutonium dioxide from stoichiometry, 2) the presence of metal impurities in the oxide fuel, 3) the formation of liquid and gaseous reaction products, as well as polymerization of the oxide products (MoO_3 , Mo_3O_9 , Mo_4O_{12} , etc.), and 4) non-equilibrium conditions make theoretical analysis of these metal container/fuel systems rather speculative.

Some of the thermodynamic and physical property data of metals and oxides that are of interest in this investigation are given in Tables 1 through 5 and Figures 2 through 4. Discrepancies exist in some of these data, so care must be taken in applying them to the systems under investigation. For example, Table 1 gives two values for the change in free energy for the reaction

One value was obtained using Glassner's⁴ compilation, and the other was obtained with Oetting's⁵ data for plutonium oxide. These calculated free energies of reaction differ not only in magnitude, but in sign as well, in the temperature range under investigation.

Partial pressures for the vapor components of plutonium dioxide as calculated from the data of Ackerman et al.⁶ are given in Table 2. It is of interest to note that the oxygen partial pressure decreases as the plutonium dioxide becomes more substoichiometric with respect to its oxygen content. For example, at 1800°K, $\text{PuO}_{2.00}$ has a calculated O_2 partial pressure of 0.29×10^{-3} atm, as compared to 0.28×10^{-7} atm for $\text{PuO}_{1.81}$.

The partial molar free energy of oxygen, $\Delta\bar{G}_{\text{O}_2}$, is plotted as a function of temperature for the $\text{PuO}_{2.00}$ - $\text{PuO}_{1.85}$ region in Figure 2.^{7,8} This figure illustrates the increased stability of plutonium oxide with decreasing oxygen content. Values of $\Delta\bar{G}_{\text{O}_2}$ for five metal/oxide systems of interest in the compatibility program are also shown in the figure. These plots suggest that if, for example, Ta_2O_5 is the reaction product for a container/plutonium dioxide test capsule, oxygen would be transferred from the fuel to the container until $\text{PuO}_{2.00}$ was reduced to between $\text{PuO}_{1.812}$ and $\text{PuO}_{1.741}$. At this point $\text{PuO}_{1.74}$ would be stable with respect to Ta_2O_5 .

Vapor pressure data for a number of oxides are listed in Table 3.⁹ These include 1) oxides of metals being evaluated as container materials and 2) oxides of the metal impurities found in the plutonium dioxide.

In reviewing these values it should be noted that vapor pressures measured by the effusion method are subject to error because of interactions between the oxide and metal Knudsen cell. This source of error is present in the compatibility tests. Interactions between the container and oxide fuel could result in vapor pressures and vapor species that differ from the pressures and vapor compositions reported in the literature.

A plot of the vapor pressure of various elements as a function of the inverse absolute temperature is shown in Figure 3. The majority of the figure is based on the compilation of Nesmeyanov¹⁰ and is extrapolated through the compatibility test temperature range.

Phase relationships between the refractory metal containers and the plutonium dioxide fuel are of primary importance in the understanding of the container/fuel interactions. A summary of the phase diagrams of PuO_2 with various materials that will be helpful to the reader has recently been published.¹¹ Table 4 summarizes the oxygen solubility limits in the refractory metals.¹²⁻¹⁴ The extensive differences in the oxygen solubility limits in the Group V elements, tantalum and niobium, and Group VI elements, molybdenum and tungsten, are readily apparent in this tabulation. Table 4 also includes a summary of the phase relationship of the metallic impurities present in the plutonium dioxide with the refractory metals. In reviewing the compatibility results it will be seen that these metallic impurities form intermetallic compounds on the container surfaces, as well as diffuse into the substrate. The limited diffusion data for these metallic impurities in refractory metals are given in Table 5.^{15,16} Diffusion coefficients for oxygen diffusion in refractory metals are plotted in Figure 4 as a function of reciprocal temperature.^{15,17}

TANTALUM

1000°C Unalloyed tantalum is susceptible to an intergranular mode of degradation when in contact with $^{238}\text{PuO}_2$ at 1000°C. Figures 5 and 6 show the appearance of the tantalum microstructure after completing 516 days at temperature. The extent of degradation that occurred in these specimens was estimated by the following procedure. First, measurements were made of the maximum depth of penetration and the depth at which the grain boundary network was completely interconnected. Second, an average of these two values was used to determine the average penetration listed below:

<u>Time at 1000°C</u> <u>(days)</u>	<u>Average Depth of Penetration</u> <u>(μm)</u>
132	99
266	261
516	304

In Figure 7, a plot of these data is fitted to the following parabolic rate equation,

$$\Delta X^2 = 4.3t + 40,000$$

where ΔX is depth of penetration in μm , and t is the time at 1000°C in hr. This equation simply illustrates a trend in the data. The information is too limited to consider it as proof that a parabolic rate law is being followed.

Electron microprobe x-ray analysis was performed on a tantalum sample that was at 1000°C for 266 days. The grain boundary product contained approximately 80 wt % tantalum with no plutonium present. This composition suggests that the reaction product is Ta_2O_5 . Electron backscatter and x-ray emission photographs of this specimen are shown in Figures 8 and 9.

Figure 7 also shows a plot of the average depth of penetration measured for tantalum that contains a 0.1 wt % yttrium addition (SGS tantalum). The behavior of this alloy was found to be very similar to unalloyed tantalum. Average depths of penetration are listed below:

<u>Time at 1000°C (days)</u>	<u>Average Depth of Penetration (μm)</u>
132	208
266	214
516	251

These data were fitted to the equation

$$\Delta X^2 = 2.2t + 35,000.$$

1200°C Tantalum was found to react with $^{238}\text{PuO}_2$ more uniformly at 1200°C than at 1000°C . Corrosion progressed by a surface oxidation mechanism and not by localized intergranular attack. Figures 10, 11, and 12 show the appearance of the tantalum after 60, 92, and 180 days of reaction, respectively. Thickness measurements of these specimens are listed in Table 6.

The initial base thicknesses of these specimens ranged between 1650 and 1720 μm . Unfortunately, individual starting thicknesses were not recorded, so finite thickness change measurements cannot be determined. The tabulation in Table 6 does indicate that the total tantalum loss was less than 200 μm in all specimens.

Figures 13 and 14 show the appearance of the reaction surface layer after 92 and 180 days at temperature. The 45- μm thick reaction layer is intact after the shorter exposure. However, only remnants of this layer are found on the 180-day specimen. Microprobe analyses of these layers are shown in Figures 15 and 16. The analyses show that plutonium is

limited to the surface layer. Iron and chromium, impurities in the $^{238}\text{PuO}_2$ fuel, are also present in the layer and have diffused into the tantalum substrate. It is of interest to note that the peak iron concentration is present next to the tantalum substrate in the 92-day specimen. However, after 180 days at temperature, plutonium is found between the substrate and the iron concentration peak. The iron probably formed an intermetallic compound on the tantalum surface during the initial stage of the exposure. [Evidence of a $\text{Ta}(\text{Fe},\text{Cr})_2$ composition is presented later.] As the tantalum surface receded during oxidation, the iron was left behind in the outermost region of the reaction product. (It is assumed that the reaction layer behaves like Ta_2O_5 , an anion defect oxide.)

1500°C Figure 17 shows the condition of a tantalum surface after being in contact with $^{238}\text{PuO}_2$ for 48 hr at 1500°C. The oxide surface layer has an observed maximum thickness of 140 μm and contains a metallic dispersion. Another corroded surface that contains remnants of the reaction product is shown in Figure 18. Photomicrographs of this particular region taken with the characteristic x-radiation intensities of various metallic elements are shown in Figures 19 through 24. These photomicrographs reveal the high concentration of tantalum and plutonium in the oxide product. Metallic impurities present in the $^{238}\text{PuO}_2$ fuel are found at the tantalum surface and are also concentrated in the metallic dispersion in the oxide. Based on electron probe analyses of this and similar specimens, the tantalum content of the oxide product approaches its solubility limit in $^{238}\text{PuO}_2$, as suggested by Batey.¹⁸ Also, the metallic dispersion in the oxide is tantalum containing minor additions of iron, chromium, and cobalt. No plutonium was detected below the tantalum surface in any of the specimens tested at 1500°C.

Meaningful reaction rate measurements could not be obtained with these specimens. The inability to retain the surface reaction products and the very thick walls used for these specimens discouraged attempts to reference the original tantalum/fuel interface. Efforts are presently being made to obtain such data by modifying the specimen design. A tantalum disc of known dimensions is now being included inside each thick-walled specimen. This disc is buried in the 0.75 g of $^{238}\text{PuO}_2$ that is loaded into each capsule. A cross section of one of these discs is shown in Figure 25. This disc had been in contact with the $^{238}\text{PuO}_2$ for 1000 hr at 1500°C. Before the exposure the thickness ranged between 1840 and 1890 μm . After testing the minimum thickness was 1830 μm . The amount of tantalum that was lost during the 1000 hr is therefore limited to 30 μm per side. The absence of any visible corrosion on this specimen suggests that very little tantalum was actually lost during the 1000-hr exposure, as implied by the thickness measurements.

Figure 26 shows the results of a hardness traverse of the tantalum disc. Surface hardening extends to a depth of about 300 μm . Hardening in this region is attributed to a combination of iron, chromium, and cobalt diffusion and oxygen contamination. (Microprobe analysis of the capsule that contained the disc showed that iron penetrated at least 120 μm into

the side wall.) The central hardness of 280-290 DPH indicates that oxygen contamination is present throughout the 1830 μm thick cross section. Fully annealed, pure tantalum would be expected to have a Vickers hardness of less than 200 DPH. These measured depths of contamination are in general agreement with the magnitudes of the diffusion coefficients. The estimated diffusion coefficients for iron and oxygen in tantalum at 1500°C are 10^{-8} to 10^{-9} cm^2/sec and 10^{-6} cm^2/sec , respectively.¹⁵ Depth of iron penetration of a few hundred micrometers would be expected. Oxygen penetration could be as much as 30 to 100 times greater than the iron penetration, depending on the concentration gradient of the diffusing elements.

1700°C An oxide reaction layer was readily visible on the tantalum surfaces after the 1700°C exposures. Figures 27 through 30 are photomicrographs of specimens tested at this temperature. The thickness of the retained oxide product was about 90 μm after 200 hr and 95 μm after 500 hr at 1700°C. Microprobe analyses showed that both tantalum and plutonium were contained in this oxide. The estimated tantalum analysis is about 10 wt %. In addition to the surface oxide, an oxide phase was also present in the tantalum substrate after the 500-hr exposure. Figure 30, the microprobe trace of this specimen, shows that plutonium is present in this oxide. One of these plutonium-containing oxide particles was located 225 μm below the tantalum surface.

Interaction of the tantalum with the metal impurities present in the fuel are readily visible in the two microprobe traverses, Figures 29 and 30. The specimen exposed for 200 hr at 1700°C shows the presence of an iron, cobalt, and chromium-rich layer on the tantalum surface. There appear to be two plateaus in the tantalum content of the surface layer at about 85 wt % and 62 wt %, the latter approaching the composition $\text{Ta}(\text{Cr}, \text{Fe}, \text{Co})_2$. (A TaMe_2 Laves phase is found in the iron, chromium, and cobalt binary systems.) The presence of silicon in the 25 μm thick intermetallic surface layer does not usually occur. Silicon is only a trace impurity in the alpha fuel. (Carbon was not present with the silicon, so contaminants from the metallographic preparation, i.e., SiC , do not explain its presence.) The probe trace of the specimen exposed for 500 hr at 1700°C indicates that the surface phase is no longer present.

Iron, chromium, and cobalt diffused into the tantalum substrate, iron being the most mobile element. The maximum depth of iron penetration was greater than 260 and 325 μm after 200 and 500 hr, respectively. Figure 31 illustrates the correlation between hardness and impurity penetration for the 500-hr specimen. Note that the hardness continues to decrease past the 325 μm distance at which the probe trace was discontinued. The iron microprobe intensity line was still greater than the background reading at this point. The relatively high hardness at 750 μm below the surface again suggests that oxygen diffused to at least this distance below the surface. This 250 DPH value is significantly greater than the hardness of annealed pure tantalum.

Discussion Tantalum was observed to undergo a series of changes in its compatibility behavior with the $^{238}\text{PuO}_2$ as the test temperature increased. First, an intergranular mechanism of corrosion was observed at 1000°C. Increasing the temperature to 1200 and 1500°C resulted in a second mode of attack, uniform surface corrosion. At temperatures of 1500°C or less, the plutonium was limited to the surface reaction products (oxides) that formed. However, increasing the temperature to 1700°C resulted in a third type of behavior, such as internal oxidation or pipe diffusion along grain edges. Oxide particles containing plutonium and tantalum formed below the tantalum surface. Diffusion of plutonium along the grain edges could explain this microstructure. When the sample is polished at and parallel to a grain edge, an elongated particle would be observed, whereas sectioning across a grain edge results in a more rounded particle. The second phase would not appear continuous in nature.

Transformation of the corrosion mechanism from intergranular to uniform surface attack as the temperature is increased is very similar to the low-pressure oxidation behavior of unalloyed tantalum. Kofstad¹⁹ observed that initial oxide formation at pressures less than 10^{-1} torr is apparently favored at grain boundaries. He reported that intergranular oxidation was severe at 1000 and 1100°C. Kofstad also noted that the oxide scale appeared more compact as the oxidation temperature increased from 1000 to 1200°C. He concluded that the scales became increasingly protective due to increased sintering and improved plastic properties of the scale above 1050°C.

In comparing the compatibility behavior of the tantalum as a function of temperature another consideration is important. The 1000 and 1200°C test capsules were "thin-walled" cylinders (0.051 cm thick). However, the 1500 and 1700°C capsules were "thick-walled" cylinders (0.528 cm thick). Differences in behavior after long exposure times would therefore be anticipated. The quantity of $^{238}\text{PuO}_2$ present in these capsules did vary, about 1.5 g at 1000 and 1200°C and 0.5 to 0.75 g at 1500 and 1700°C. However, the internal surface areas of these specimens were such that the weight of fuel per unit surface area was 0.35 g/cm² for all temperatures. This value was used as a basis for the calculations given below. These calculations also include another variable, the amount of metal impurities present in the fuel, 1 wt % and 0.5 wt % total metal impurity. It was assumed that the metal impurities were present as MeO, Me being iron, cobalt or nickel (at. wt of Me ~ 58 g/g-mole). This assumption makes the potential for oxidation of the tantalum higher than if it is assumed that the oxide fuel is only $^{238}\text{PuO}_2$. Based on thermodynamic calculation, it is expected that 1) the tantalum getters all oxygen from the MeO and 2) tantalum reduces PuO_2 to the composition $\text{PuO}_{1.74}$. At the latter oxide composition, the plutonium oxide is more stable than Ta_2O_5 , and no further reduction will occur. Figure 2 shows the free-energy relationships that justify the latter assumption. The following results were obtained based on the above assumptions:

- A. Amount of oxygen available for reacting with the tantalum container

$6.7 \times 10^{-3} \text{ g/cm}^2$ * for 1% Me impurity fuel
 $6.3 \times 10^{-3} \text{ g/cm}^2$ for 0.5% Me impurity fuel

- B. Oxygen content of tantalum if completely dissolved in the metal

Thin-walled capsule

0.79 wt % for 1% Me impurities in fuel**
0.73 wt % for 0.5% Me impurities in fuel

Note: This exceeds the solubility limit of oxygen in tantalum
at 1000°C (0.26 wt %) and 1500°C (0.37 wt %).

Thick-walled capsule

~ 0.08 wt % for 1% Me impurities in fuel
~ 0.07 wt % for 0.5% Me impurities in fuel

Note: Even though all oxygen is capable of dissolving in the tantalum, the diffusion rate of oxygen is probably less than the surface reaction rate to form a surface oxide, as is true for tantalum oxidation at these temperatures. An oxide surface layer does form, although after an extended period of time dissolution of the oxide could occur.

- C. Amount of tantalum consumed if all oxygen was used to form a surface reaction layer.

19 μm for 1% Me impurities in fuel
17 μm for 0.5% Me impurities in fuel

- D. Thickness of surface reaction layer if all oxygen was used to form this layer:

If layer Ta_2O_5 ,

45 μm for 1% Me impurities in fuel
41 μm for 0.5% Me impurities in fuel

If layer $\text{PuO}_2 \cdot 2\text{Ta}_2\text{O}_5$

58 μm for 1% Me impurities in fuel
52 μm for 0.5% Me impurities in fuel

(Complex oxide formation suggested by results shown in Figure 16.)

*Grams of oxygen per cm^2 of internal capsule surface area.

**Volume $\approx$ (internal surface area) (thickness); error in volume of right circular cylinder is neglected for small values of thickness.

If layer is PuO_2 containing 20 wt % Ta in solid solution

140 μm for 1% Me impurities in fuel

130 μm for 0.5% Me impurities in fuel

(Solution of Ta in a Pu-rich oxide is suggested by Figures 25 and 26.)

The above calculations suggest that there is a limited source of oxygen available to react with the tantalum container in this study. Even with this limited source, the thin-walled capsules can suffer extensive degradation, especially if the oxygen concentrates at grain boundaries as was observed in the 1000°C studies. The inability to measure any extensive surface recession at 1200 and 1500°C becomes apparent when the above calculations suggest that only about 20 μm of tantalum will be depleted if uniform surface corrosion does occur. The measured oxide thickness of 45 to 140 μm at 1200 through 1700°C and the approximate tantalum contents of the oxide reaction products tend to verify these thickness calculations.

The extent of tantalum oxidation in a closed system would be a function of the amount of oxide fuel present inside the system, if the tantalum-plutonium oxide reaction is oxygen limited. As the internal capsule volume and volume of fuel increase, more tantalum could be consumed by oxidation. This effect is illustrated by Figure 32. The basis for the tantalum-loss curves is similar to the previous calculations. It was assumed that 1) the fuel contained 0.5 wt % metal impurities as MeO , 2) the $\text{PuO}_{2.00}$ was reduced to $\text{PuO}_{1.74}$, 3) the tantalum was completely saturated with oxygen, and 4) Ta_2O_5 was the oxide product. Figure 32 shows that appreciable tantalum could be consumed by oxidation, as the capsule diameter (the fuel supply) is increased. This potential for oxidation could presumably be decreased by using a substoichiometric plutonium oxide fuel.

There are objections to the supposition that the $^{238}\text{PuO}_2$ /tantalum reaction is oxygen limited. The oxide Ta_2O_5 can become unstable at low oxygen partial pressures. Decomposition can occur and serve as an oxygen source. The gaseous oxides TaO and TaO_2 can form at very high temperatures and low oxygen pressures. Thus, a mode for mass transport of tantalum away from the container surface can be conceived. Decomposition of these gaseous oxides at some favorable site could deposit tantalum in the $^{238}\text{PuO}_2$, for example, and free additional oxygen into the system. Examples of such gaseous oxide decomposition and metal deposition are presented in the molybdenum and tungsten sections of this report. It should be noted that no concrete evidence of the vapor transport of tantalum in a tantalum system was observed.

Impurities present in the $^{238}\text{PuO}_2$ are an important variable in the compatibility behavior of tantalum. Diffusion of these elements into the tantalum and the formation of surface compounds such as TaFe_2 change the capsule's surface composition. This in turn would affect the composition and rate of formation of the fuel/capsule reaction products. Such

impurities could be beneficial if they decrease the reaction rates, by forming a protective layer for example. Detrimental effects could occur as well, if they form low melting reaction products. Additional work is required in this area before such effects are clearly defined.

TANTALUM-10 WT % TUNGSTEN

1000°C Tantalum-10 wt % tungsten was found to be less susceptible to intergranular attack than tantalum at 1000°C. Figure 33 shows the appearance of the alloy after 516 days of testing. Summarized below are the average depth of intergranular penetration found in tantalum-10 wt % tungsten:

<u>Time at 1000°C</u> <u>(days)</u>	<u>Average Penetration</u> <u>(μm)</u>
132	54
266	63
516	77

A penetration rate curve for the alloy is shown in Figure 34. The data can be approximated by the equation:

$$\Delta X^2 = 0.33 t + 1,800$$

where t is time in hr, and ΔX is the depth of penetration in μm .

1200°C Intergranular attack of the tantalum-10 wt % tungsten substantially increased over that observed at 1000°C. Figures 35 and 36 are duplicate samples and show the appearance of the base of a capsule after 360 days at 1200°C. The corrosion consists of a 35 μm thick, surface oxide layer in addition to the oxide present in the grain boundaries. Microprobe analysis of one of these specimens showed that plutonium is present only in the surface oxide. A ternary Pu-Ta-O compound is suggested by the data. The microprobe analysis also indicates that the stratified appearance of the oxide surface layer is the result of variations in the metal contents of the oxide. Figure 37 gives the microprobe trace, and Figures 38-43 are photomicrographs taken with backscattered electrons and characteristic x-radiation of plutonium, tantalum, tungsten, chromium, and iron, which illustrate these concentration variations. The oxide present in the grain boundaries is thought to be Ta_2O_5 , based on the approximate tantalum analysis. A small amount of chromium appears to be present in this oxide at the 75 μm reference distance of Figure 37.

Surface recession of the tantalum-10 wt % tungsten was negligible at 1200°C. The nominal 1000 μm starting thickness of the capsule base showed no measurable change after the thermal exposure for any of the specimens. The depth of intergranular attack was erratic and could not be correlated with a rate constant. Comparison of Figure 44 to Figure 37 illustrates the differences in corrosion that occurred in the two specimens heated for 360 days. One specimen shows apparently complete (1000 μm) intergranular penetration of the base as compared to 50 μm penetration in the duplicate specimen.

The magnitude of the corrosion varied within the capsules. The base of the capsules were most severely degraded, whereas the cylindrical walls in contact with the fuel were generally less corroded. Cylindrical walls not in direct contact with the $^{238}\text{PuO}_2$ showed no appreciable microstructural changes. (These capsules were about half filled with $^{238}\text{PuO}_2$.)

Variable Impurity Studies at 1200°C The effect of metal impurities in the $^{238}\text{PuO}_2$ on the compatibility of tantalum-10 wt % tungsten was extensively evaluated at 1200°C. A high purity fuel was especially processed for this study. Controlled amounts of iron and chromium were then added to it. The particular compositions that were investigated are given in Table 7.

Tantalum-10 wt % tungsten capsules containing these fuel compositions were exposed for 30, 60, and 120 days at temperature with the exception of the base composition.

Table 8 summarizes the microprobe analyses of these specimens. Figure 45 shows a typical microprobe traverse. A thin, intermetallic layer formed on the surface of the tantalum-10 wt % tungsten that contacted the fuel. A photomicrograph taken at higher magnification is shown in Figure 46. Based on an approximate tantalum analysis, this phase is thought to be $\text{Ta}(\text{Cr}, \text{Fe})_2$. (An AB_2 Laves phase is present in the Ta-Cr and Ta-Fe binary systems.) Depth of iron diffusion into the alloy is greater than that of chromium, as would be expected from the higher melting point of chromium. Intergranular oxidation caused more degradation to the substrate than the fuel impurity reactions. Figures 47 and 48 are photomicrographs of this intergranular attack. Chromium was detected in some of these grain boundaries to a depth of 150 μm below the alloy surface. A summary of the metallographically measured depths of intergranular penetration are given in Table 8.

External surfaces of the majority of the tantalum-10 wt % tungsten capsules showed indications of contamination and localized oxidation. Figure 49 is a photograph of one of these regions. (Molybdenum or tungsten foil is present between the surfaces and the inner surface of the Hastelloy-X outer capsule. The test capsule is electron-beam weld sealed inside the outer capsule.) Chromium vaporization from the Hastelloy-X is a possible source of some of the contamination. But it is suspected that oxygen diffusing through the grain boundaries of the tantalum-10 wt % tungsten, or through cracks in the tantalum-10 wt % tungsten test capsule, is causing much of the external contamination. Diffusion of oxygen through Hastelloy-X is feasible. However, outgassing of the oxygen from this alloy into the inner void volume does not appear to be thermodynamically favorable. (An oxygen pressure less than 10^{-16} torr might be necessary before outgassing of the Hastelloy-X can occur. This pressure is the equilibrium oxygen pressure of Cr_2O_3 , as chromium is a major constituent of this alloy.) Some of this external oxidation might also have resulted during the TIG-welding operation if the inert welding atmosphere was contaminated with oxygen.

1500°C The appearance of a tantalum-10 wt % tungsten surface after being in contact with $^{238}\text{PuO}_2$ for 96 hr at 1500°C is shown in Figure 50. Surface and intergranular attack are readily visible in the photomicrograph. Microprobe analyses identified iron, cobalt, and chromium in the 50 μm thick porous surface layer. A high concentration of these impurities is present in a narrow zone just below this porous layer. The analyses also show that these metal impurities diffused an additional 150 μm into the tantalum-10 wt % tungsten below this peak concentration.

A longer exposure at 1500°C, 200 hr, resulted in the formation of a mixed metal and oxide surface layer, as shown in Figure 51. This 75 μm thick surface layer contains plutonium along with tantalum, tungsten, iron, cobalt, and chromium. Iron, cobalt, and chromium were detected to a depth of an additional 75 μm . No intergranular corrosion was observed in this specimen.

A series of hardness measurements that were obtained from these specimens is shown in Figure 52. Surface hardening did result from the metallic impurities and oxygen contamination. Depth of surface hardening was about 200 μm after 48 to 96 hr at temperature, increasing to a maximum of 300 μm for the longer exposures. The apparent increase in the base hardness of the 500-hr and 1000-hr specimens could be an indication of more extensive contamination than the 200 to 300 μm deep increase in hardness. Solution of oxygen in the tantalum-10 wt % tungsten is suspected. It should be noted that these depths of penetration are referenced with respect to the specimen surface. This surface is not necessarily the original metal/fuel interface. (The particular specimen design did not permit any surface recession measurements to be made.) Much of the scatter in the data undoubtedly came from the fact that no precautions were taken to avoid hardness measurements at grain boundaries, which are known to be harder than grain interiors.

1700°C A photomicrograph of the surface of tantalum-10 wt % tungsten after 48 hr in contact with $^{238}\text{PuO}_2$ at 1700°C is shown in Figure 53. An oxide phase can be seen dispersed throughout the alloy. In addition, a layer of fuel next to the alloy surface contains a dispersion of spherical metal particles.

Electron microprobe analyses of the specimens tested at 1700°C showed substantial amounts of plutonium present in the oxide precipitates. The composition of these oxide precipitates in the alloy and the composition of the oxide next to the alloy surface were very similar. An estimate of the tantalum composition of this oxide is about 15 wt %. The metal precipitate in the bulk oxide is primarily the tantalum-tungsten alloy containing substantial additions of iron, cobalt, nickel, and chromium. Figure 54 is a typical microprobe trace that illustrates the features of this metal/oxide reaction at 1700°C. Figures 55 through 59 are photomicrographs of the reaction layer taken with the characteristic x-radiation lines of the elements of interest. Figure 60 is a low magnification photomicrograph of the alloy showing the extensive oxide penetration that was observed after 1000 hr at temperature.

It is of interest to note that the features of this reaction are also similar to the observations of Batey et al. on the Ta-Pu-O system.¹⁸ They also observed a tantalum-plutonium oxide and a spherical tantalum metal precipitate in the oxide.

Depth of oxide penetration into the tantalum-10 wt % tungsten was measured for five different exposure times. The results of these measurements are given in Table 9.

2500°C Tantalum-10 wt % tungsten was heated in contact with liquid $^{238}\text{PuO}_2$ for 5 min at 2500°C. Figure 61 shows the capsule design used in this experiment. Approximately 8 min were required for the sample to reach 2000°C and another 1.5 min to reach 2500°C. While the capsule was at temperature the top disc sank and bonded to the bottom disc. The end caps of the capsule bulged outward as the result of the internal pressure buildup, and liquid plutonium then flowed under the bottom tantalum-10 wt % tungsten test disc. Figure 62 is a photomicrograph of the two tantalum-10 wt % tungsten discs after they were removed from the capsule.

Measurements of the thickness of the two discs indicated that 41 to 112 μm of the alloy were removed by dissolution in the liquid $^{238}\text{PuO}_2$. Metal dendrites were found in the resolidified fuel. This indicates that tantalum had dissolved in the liquid $^{238}\text{PuO}_2$ and precipitated out on cooling. Figure 63 is a photomicrograph of the reaction zone showing these dendrites. The results of the microprobe analyses are also shown in this figure.

Diffusion of iron, cobalt, and chromium into the tantalum-10 wt % tungsten alloy was detected in the microprobe analysis. These impurities were also concentrated in the alloy grain boundaries in localized areas. The dendrites were primarily tantalum and contained some chromium, iron, and cobalt.

Discussion The compatibility behavior of tantalum-10 wt % tungsten and $^{238}\text{PuO}_2$ varies extensively with the reaction temperature. Intergranular penetration is not excessive at 1000°C, less than 100 μm (4 mils) in 516 days. However, increasing the reaction temperature to 1150-1200°C results in a substantial increase in intergranular attack. One hundred micrometers of corrosion occurred within 120 days at this higher temperature. Examples of 1000 μm of intergranular attack were observed after one year at 1150-1200°C. Although more quantitative data are not presently available for the 1500°C reaction temperature, metallographic results suggest that the incompatibility between tantalum-10 wt % tungsten and $^{238}\text{PuO}_2$ becomes less severe. Increasing the reaction temperature to 1700°C again results in extensive intergranular attack and possible internal oxidation.

Electron microprobe data show that plutonium does not diffuse into the alloy at temperatures as high as 1500°C. This element is found only in the surface reaction product until the 1700°C reaction temperature is reached. At 1700°C, a tantalum-plutonium oxide is found dispersed in the alloy. The analyses also show that dissolution of tantalum in $^{238}\text{PuO}_2$ can occur at 1700 and 2500°C.

Metallic impurities found in the production grade $^{238}\text{PuO}_2$ contribute to the compatibility reaction. The elements iron, cobalt, nickel, and chromium can form intermetallic compounds on the alloy surface. These elements also diffuse into the tantalum-10 wt % tungsten increasing its hardness. Traces of these elements, especially chromium, were detected in the tantalum oxide that forms in grain boundaries at the 1150-1200°C reaction temperature range. In the test results obtained at 1150-1200°C, it appears that even when these impurities are reduced to less than 0.1 wt % intergranular attack will still occur.

T-111(222) ALLOY

T-222 at 1000°C At 1000°C, T-222 showed less reaction than either tantalum or tantalum-10 wt % tungsten alloy, although the nature of the reactions were similar. A photomicrograph of T-222 after exposure for 532 days at 1000°C is shown in Figure 64. An intergranular reaction product is seen to a depth of about 26 μm . The depth of penetration data obtained on these samples are summarized in Table 10. These data are plotted in Figure 65. The equation calculated from this line is $\Delta X^2 = 0.055t$ where ΔX is the penetration in micrometers and t is the time in hours. The parabolic rate law is assumed to apply in this case although at this point the data are insufficient to prove whether this type of relationship is operative.

T-222 at 1200°C Tests were conducted with T-222 at 1200°C for 40, 60, 90, and 180 days. Photomicrographs of 60- and 90-day samples are shown in Figures 66 and 67, respectively. From these photomicrographs it is obvious that intergranular attack takes place, along with a more general attack at the reaction interface. The surface reaction product appears to be porous and somewhat friable in nature. In addition to the intergranular reaction product, the alloy is quite brittle as indicated by the cracks throughout the samples. These capsules tended to shatter when handled after testing. Also, in Figure 67, whole grains appear to have popped out of the surface of the sample.

Some of the embrittlement may have been caused by a poor welding atmosphere at the time of welding. Difficulty was encountered in welding some of the samples, which is indicative of a poor welding atmosphere. However, this effect should be confined to the end of the capsule opposite the fuel and not the fuel end, so that the contribution from this source should be low. The fuel, however, is responsible for much of the embrittlement since the vast majority of the intergranular oxidation occurred along the fuel-metal interface.

A summary of the quantitative measurements obtained from these samples is given in Table 11. Measurements are given for both the general layer and the intergranular reaction product. The data are plotted in Figure 68. It can be seen from Table 11 and Figure 68 that there is considerable scatter in the data. This is due partly to the fact that considerable difficulty is encountered in trying to determine maximum penetration; the fact that some of the intergranular attack seemed to be localized;

and the fact that the surface layer seemed to be rather friable and flaked off readily. This is probably the reason for the large deviation for the 4320-hr, general reaction layer point. In spite of this large scatter the equations for these liners were calculated to be $\Delta X^2 = 6.35t - 6000$ for the general reaction and $\Delta X^2 = 4t + 8000$ for the intergranular reaction, where ΔX is the penetration in micrometers and t is the time, in hours. Attempts are being made, by refining the test procedure, to improve the data so that a better rate constant can be obtained.

A photomicrograph and trace of the electron microprobe strip chart analysis of a sample tested for 90 days is shown in Figure 69. The microprobe data are typical of results obtained on the 40-, 60-, and 90-day tests. A reaction layer 85-90 μm thick is indicated. This reaction layer shows a gradually decreasing plutonium content and increasing tantalum content when proceeding from the fuel-reaction layer interface toward the parent material. A 30-35 μm wide impurity layer is also seen on the inside edge of the wider reaction zone. This layer contains chromium, iron, cobalt, aluminum, a small amount of nickel, and tungsten.

A slightly different appearing reaction interface is shown in Figures 70 and 71, which show a photomicrograph and a trace of the x-ray strip chart analysis of a 180-day sample. This specimen shows a 25- μm wide, light-phase reaction zone along the interface, similar to that shown in Figure 69. This zone contains the fuel impurities iron, chromium, nickel, and cobalt, and an increased tungsten content. This layer contains approximately 55 wt % tantalum which suggests a $\text{Ta}(\text{Fe}, \text{Cr}, \text{Co}, \text{Ni})_2$ intermetallic compound. The gray phase in this region contains hafnium and plutonium.

A trace of the electron microprobe strip chart analysis of the grain boundary product is given in Figure 71. The central, dark gray portion of the grain boundary product contains plutonium and some hafnium. Fuel impurities are found in the light gray phase on either side of the plutonium layer.

T-111 at 1500°C Data are available for only one sample tested at 1500°C. An intergranular reaction product was found to a maximum depth of 590 μm after 1000 hr. Electron microprobe analysis show this product to contain hafnium and plutonium. Iron was found to diffuse into the alloy to a depth of about 550 μm , and chromium diffused to about 350 μm . In addition a 50-60 μm reduction in thickness of the disc was observed.

T-111 at 1700°C Tests were conducted with T-111 alloy at 1700°C for 24, 48, 200, 500, and 1000 hr. Metallographic and electron microprobe data show a reaction between the fuel and the alloy which is progressive with time. Figure 72 is a photomicrograph of a 24-hr sample. Electron microprobe analysis shows that the gray particles contain hafnium and plutonium. The reaction has progressed to a depth of approximately 40 μm . Presumably oxygen from the fuel forms HfO_2 which then combines with PuO_2 . The concept of fuel decomposition as a source of oxygen is supported by the fact that x-ray analysis of the fuel after testing at 1500 and 1700°C shows the presence of two phases, PuO_2 and hexagonal Pu_2O_3 .

A photomicrograph and trace of the electron microprobe strip chart analysis of a 48-hr sample are given in Figure 73. This figure shows the progression of the intergranular reaction product to a depth of 80-100 μm followed by a general reaction between the fuel impurities and tantalum along the fuel-alloy interface to a depth of 16-28 μm . The electron microprobe data show that the light-phase reaction layer consists of decreased tantalum and tungsten with iron, chromium, and cobalt. In addition, there is a general though less evident diffusion of iron to 140 μm and chromium to 125 μm . Tungsten is also seen to be increased over the base composition along the interface between the impurity reaction layer and the parent material. The dark gray particles in the grain boundaries contain plutonium and hafnium.

Photomicrographs of samples tested for 200, 500, and 1000 hr indicate that a loss of the impurity-alloy reaction layer into the fuel begins between 48 and 200 hr. The plutonium plus hafnium penetration continues through 1000 hr. Tungsten-enriched particles are also lost from the surface of the alloy into the fuel. This is shown in Figure 74 which gives a photomicrograph and a trace of the electron microprobe strip chart analysis. The dark gray phase in area "C" has not yet been identified.

Depth of penetration measurements for T-111 at 1700°C are given in Table 12. The values for 500 and 1000 hr are less than expected. This is no doubt due to recession of the interface as indicated by Figure 74. The capsule design did not permit measurements of surface recession. A rate curve for the data in Table 12 is given in Figure 75. The data for 500 and 1000 hr are not included in this figure. The equation for the line obtained is $\Delta X^2 = 230t - 4500$ where ΔX is the penetration in micrometers and t is the time in hours.

Discussion Intergranular oxidation seems to be the most common reaction on T-111(222) between 1000 and 1700°C. At 1200°C and above, hafnium in the grain boundaries appears to oxidize and interact with plutonium (presumably PuO_2). No electron microprobe data are available for the 1000°C tests. Rate equations of a sort were obtained at 1000, 1200, and 1700°C. Figure 76 is a plot of the logarithm of the rate constant as a function of reciprocal temperature. The agreement between the points is reasonable, considering the scatter in some of the data, particularly at 1200°C. It is also possible that a change in mechanism could be taking place which could result in a change in activation energy. At lower temperatures, 1000-1200°C, the activation energy is approximately 80 kcal/mole, whereas between 1200 and 1700°C the activation energy is approximately 46 kcal/mole. The rate constants used in this figure are based on the general relationship $\Delta X^2 = 2kt + C$ where ΔX is the reaction depth in micrometers, k is the reaction rate constant, t is the time in hours, and C is a constant. Until more reliable data are available Figure 76 should be used with caution. Tests are under way which should improve the accuracy of the data.

Severe embrittlement of T-111 or T-222 results at all temperatures, presumably because of oxygen absorption. The presence of hafnium seems to be detrimental to T-111 at higher temperatures because of the formation of hafnium-plutonium (and presumably oxygen) reaction products.

NIOBIUM

1500°C After exposure for 12 hr at 1500°C, the reaction between $^{238}\text{PuO}_2$ and niobium appeared to be intergranular in nature. This is shown in Figure 77. A niobium-plutonium reaction product (oxygen is also probably present) is observed discontinuously below the reaction interface. This is illustrated more clearly in Figure 78, which shows a sample exposed for 24 hr. Photomicrographs taken with backscattered electrons and with the characteristic x-rays of plutonium are shown in Figures 79 and 80. These figures show that the intergranular reaction contains plutonium, although no measurement of relative amounts of plutonium and niobium are possible.

After 96 hr, a different type of reaction is indicated as shown in Figure 81. This photomicrograph shows the region between the pin and the sidewall, where fuel has been retained at the edge of the niobium. Small white particles which were identified as niobium are seen in the fuel, and some are seen emanating from the metal itself. This structure suggests the presence of a liquid phase, or the solubility of niobium in solid PuO_2 , and subsequent precipitation upon cooling. (The melting point of Nb_2O_5 is approximately 1460°C, which is below the temperature of these tests.) If Nb_2O_5 forms and melts at the interface, it can react with both PuO_2 and niobium, forming a solution. Upon cooling, the niobium could solidify in the manner indicated. Unfortunately, this type of attack does not permit quantitative measurements because of the uncertainty of the original interface.

Microhardness measurements across the reaction interface for a 375-hr sample are shown in Figure 82. There is a fair amount of scatter in the data that is probably caused by the random nature of the measurements. No attempt was made to position the sample so that measurements would be made at the center of a given grain. Therefore it is probable that many of the measurements were made across grain boundaries, which would result in slightly higher values. The microhardness values reach a minimum of about 171 VHN at about 500 μm from the interface. Figure 83 shows the square of the distance from the interface of this leveling off for all the samples tested. With the exception of the 168-hr test, the data fit a standard rate curve. The equation for the upper portion of the curve is

$$\Delta X^2 = 300 t + 200,000$$

where ΔX is in micrometers and t is the time in hours. At the same time, the minimum microhardness values tend to increase with increasing exposure time. This is shown in Figure 84 which shows the minimum microhardness values as a function of $\sqrt{t}$. In this case two points deviate considerably from the rest, but in general, the values increase with time. Attempts to correlate these microhardness data with impurity diffusion have proved fruitless. However, Tottle²⁰ has shown that the microhardness of niobium increases with increasing oxygen content. If oxygen absorption is responsible for the hardness increase at the reaction interface, this would explain the large values obtained for ΔX^2 in Figure 83.

1700°C At 1700°C a structure that is best described as a eutectic structure is obtained. This is shown in Figure 85 which shows a sample exposed for 24 hr. The white phase is niobium, which is consistent with the fact that many of these particles are seen originating from the base metal. A trace of an electron microprobe strip chart analysis of this sample is given in Figure 86. Chromium is also found to be associated with the niobium particles. The niobium content of the fuel is also seen to be very low, although there appears to be a small amount.

Further evidence in support of a liquid phase is shown in Figure 87, which shows a photomicrograph of a 168-hr sample. Again electron microprobe analysis indicates very little niobium content in the fuel. However the presence of a liquid phase appears to be the only way a structure of this type could originate. No microhardness data were obtained on samples exposed at 1700°C.

Discussion From these results it is obvious that at 1500 and 1700°C, $^{238}\text{PuO}_2$ and niobium are incompatible. Solution of niobium by the fuel is apparent. A general attack of the surface results. As the sample cools, the niobium is precipitated from solution, forming a eutectic-like structure. The exact nature of this matrix phase is unknown, although it appears to contain very little niobium at room temperature. Unfortunately this general solution type of reaction precludes quantitative measurements of reaction rates for samples of this design.

Microhardness measurements show an appreciable hardness increase at the surface. It is believed that this hardness increase is due to solution of interstitials (primarily oxygen) rather than solution of impurities. This is consistent with the fact that the maximum solid solubility of oxygen in niobium is approximately 4 at. % at 1915°C.¹³

MOLYBDENUM

1200°C A photomicrograph of the reaction interface of molybdenum after 60 days at 1200°C is shown in Figure 88. A layer of reaction product is seen approximately 14 μm below the interface. Photomicrographs taken with backscattered electrons and with the characteristic x-rays of iron, cobalt, plutonium, and molybdenum are shown in Figures 89-93. From these photomicrographs it can be seen that the reaction product consists of plutonium in conjunction with fuel impurities of iron and cobalt. A small amount of silicon is also found in these areas. The region between the edge of the sample and the reaction product line (0-14 μm) is primarily molybdenum with impurities (iron and cobalt) in solution. A trace of an electron microprobe strip chart analysis across this area is shown in Figure 94. Two observations can be made from this strip chart. The first is that the iron and cobalt concentration across this region is reasonably constant, and the second is that peaks occur 60, 110, 150, and 200 μm from the reaction interface, suggesting preferential grain boundary diffusion of impurities.

The results of 180 days of exposure at 1200°C are shown in Figures 95-102. Figures 95 and 96 are optical photomicrographs of the reaction interface, and Figures 97-102 are photomicrographs taken with backscattered electrons and the characteristic x-rays of molybdenum, plutonium, cobalt, iron, and chromium, respectively. In addition, a trace of the x-ray strip chart analysis is given in Figure 103. From these figures it can be seen that plutonium remains concentrated on the surface of the molybdenum with no detectable diffusion inward. The apparent porosity at the interface of Figure 95 cannot be explained at this time, although it appears to be associated with impurities. Superimposed on the microprobe traces in Figure 103 is a microhardness traverse across this same area. From this traverse it is obvious that there is a considerable increase in hardness as a result of the presence of these impurities. Higher microhardness values are also obtained at the grain boundaries where the iron and chromium content is highest. A summary of the depth of penetration of the impurities is given in Table 13. Since the data are somewhat erratic it is possible that at the longer time periods the impurity reaction layer is flaking off.

1500°C A photomicrograph of the reaction interface after 48 hr at 1500°C is shown in Figure 104. In this figure the fuel is shown to be separated from the molybdenum by a large gap which has filled with mounting material. A few particles can be seen adhering to the molybdenum, although it is not known unequivocally whether these are fuel particles. Figure 105 shows a corner of the 200-hr sample between the plug and the sidewall. A small amount of fuel is observed between the two pieces, and small fingers of metal are seen emanating from each piece, suggesting a mass transport phenomenon. A trace of the electron microprobe strip chart analysis of this sample between the plug and the sidewall is shown in Figure 106. Fuel particles are shown as well as fingers of molybdenum emanating from either side. Impurities are observed on either reaction interface, although no molybdenum is observed in the fuel.

Mass transfer is also indicated in Figure 107 which shows the corner between the plug and the sidewall on a sample annealed for 500 hr. The material in this sample migrated far enough that interlocking of the two pieces appears to be taking place. If this morphology was due to attack by PuO_2 , interlocking would not be expected. Instead, recession of the surface at selected regions might be observed, but the fingers of metal would not project beyond the original interface.

A different type of structure is shown in Figure 108 which is a trace of an x-ray strip chart analysis of a 1000-hr sample. In this case the molybdenum can be seen intermingled with fuel particles, but this whole mass appears physically separated from the main body of metal. The photomicrograph was taken at the welded edge of the plug, and the large circular void is apparently a welding defect. The reason for separation of these two masses is unknown at this time, although it is believed that impurity reactions are responsible. The microprobe traces strongly indicate the presence of impurities. It should be kept in mind that mass transport may also be responsible for this structure, and that the appearance of the impurities is incidental to the situation.

In view of the unusual nature of these observations, primarily with respect to the mass transport phenomenon, it is not possible to give any reaction rates for these interactions. However, it should be pointed out that in no case was there any indication of direct reaction between molybdenum and PuO_2 at 1500°C .

1700°C At 1700°C the results were similar to those obtained at 1500°C , although the amount of mass transport was greater. Typical photomicrographs are shown in Figures 109-111 which show samples exposed for 12, 24, and 96 hr, respectively. Figures 110 and 111 were taken between the plug and the sidewall, and these figures show that molybdenum completely bridged the gap between them. The width of this gap is about $90\text{ }\mu\text{m}$. The extent of mass transport is further indicated by Figure 112 which shows an individual fuel particle surrounded on three sides by molybdenum. Molybdenum was also found elsewhere in the fuel.

A trace of the electron microprobe strip chart analysis of the sample shown in Figure 111 is shown in Figure 113. The results obtained on this sample are typical of those obtained at other time periods. Photomicrographs taken with backscattered electrons and the characteristic x-rays of chromium, manganese, iron, cobalt, silicon, molybdenum, and plutonium are given in Figures 114-121. Areas of high chromium, manganese, and silicon content are shown as well as a more general distribution of iron and cobalt.

At 1000 hr the results shown in Figures 122 and 123 were obtained. Dark gray particles were found to a depth of $300\text{ }\mu\text{m}$ from the reaction interface. In Figure 122 an obvious grain boundary penetration is indicated at the surface. In Figure 123 grain boundary precipitates are also indicated although there appears to be no continuity between the particles. These particles were observed in all parts of the sample. In samples treated for shorter time periods, similar precipitates were observed although rarely. Photomicrographs taken with backscattered electrons, sample current, and plutonium $\text{M}\alpha$ x-rays are shown in Figures 124-126. In the sample-current photomicrographs the light areas indicate voids. Figure 126 shows the dark gray particles contain plutonium. No other elements were found to any extent. The distribution of iron, chromium, and cobalt was found to be fairly constant, although it gradually decreased away from the reaction interface.

Apparently the plutonium (presumably PuO_2) diffuses down the grain edges and not along the faces of the grains. This mechanism would explain the morphology of the structure shown in Figures 122 and 123. When the sample is polished at and parallel to a grain edge, the plutonium phase is observed as an elongated particle as in Figure 122. Sectioning across a grain edge results in a more rounded particle.

1900°C Tests at 1900°C yielded results that are, in general, similar to those at 1700°C . The primary differences are in the degree of reaction. A considerable amount of molybdenum was found in the grain boundaries of the fuel of a sample exposed for 25 hr, as shown in Figure 127. A third,

more continuous phase at the grain boundaries is also indicated. An enlarged view of the grain boundary region, shown in Figure 128, shows that the third phase is actually a eutectic constituent. Figures 129-132 are photomicrographs taken with backscattered electrons and the characteristic x-rays of chromium, silicon, and plutonium. These photomicrographs show this eutectic to contain chromium and silicon as well as plutonium. Some chromium is also found in the large, rounded, molybdenum particle.

The fuel-molybdenum interface is shown in Figure 133. The surface is relatively smooth indicating a general removal of molybdenum from the surface, although some preference for the grain boundaries is indicated. Samples tested at 50 and 100 hr show essentially the same results. A 500-hr sample, shown in Figure 134, shows a small amount of intergranular reaction product at the reaction interface. Although no electron microprobe results are available, this intergranular product probably contains plutonium as in the 1700°C results.

Discussion The results of these tests between $^{238}\text{PuO}_2$ and molybdenum indicated three different types of reactions:

1. Reactions with impurities.
2. Mass transfer.
3. Grain boundary penetration by PuO_2 .

Reactions with impurities considerably complicate the interpretation of the results, because it is difficult to separate impurity effects from incompatibility effects. At lower temperatures the impurities tend to penetrate the grain boundaries and promote the flaking off of the surface layer. This flaking presumably occurs because of embrittlement of the surface layer by the impurities.

Some attempt was made to correlate microhardness measurements with impurity concentration. The results of one such analysis is given in Figure 103, and another is given in Figure 135. In these cases the correlation is excellent. The microhardness increases drastically near the surface compared to the values at the interior of the sample. In general, as the test temperature increases the microhardness near the reaction interface increases. At 1200°C the microhardness values approach 700 VHN at the surface; at 1500°C they approach 800 VHN; and at 1700°C they approach 950 VHN. The microhardness at the interior varies between 200 and 300 VHN. Presumably this is caused by an increased amount of impurities in solution and consequently a greater amount of solution hardening. From the viewpoint of these hardening effects, impurities in the fuel are undesirable and could lead to embrittlement of molybdenum containers.

Mass transfer effects present a different type of problem. Presumably metal is being removed from the surface and transported to another part of the capsule. Unless this transport can be controlled serious problems could result.

The mechanism of this mass transport no doubt involves molybdenum oxide, MoO_3 . At elevated temperatures PuO_2 dissociates into PuO_{2-x} and free oxygen. The oxygen can then react with molybdenum according to the reaction:

However, the boiling point of MoO_3 is reported to be 1100°C ,²¹ which means that because of the high vapor pressure of MoO_3 , equilibrium will be established very quickly. As a result very little molybdenum is oxidized. However, even a small temperature gradient could cause the reaction to shift to the left resulting in the deposition of molybdenum. The oxygen thus released could then be available to react with the molybdenum. The net result of this would be mass transfer of molybdenum from one part of the container to another.

The diffusion of plutonium along the grain edges is somewhat puzzling. Thermodynamically there should be no direct reaction between PuO_2 and molybdenum. Electron microprobe data are incomplete at this time, and it is possible that when this information is complete, a mechanism can be postulated.

TZM ALLOY

1200°C The reaction interface of TZM after 32 days at 1200°C is shown in Figure 136. A row of fine particles is observed approximately $26\text{ }\mu\text{m}$ below the surface. Also, a large, metallic-appearing particle is observed to extend out from the surface. It is not known if this particle came from the cut-off process, mass transfer as in the case of molybdenum, or from attack of the remainder of the surface away from this region. A similar result after 62 days is shown in Figure 137. Photomicrographs taken with backscattered electrons and the characteristic x-rays of plutonium, titanium, molybdenum, and chromium are shown in Figures 138-142, respectively. Concentration of plutonium and titanium are seen near the interface. In addition, appreciable amounts of cobalt and chromium were found to have diffused into the alloy.

A trace of the electron microprobe strip chart analysis of a sample exposed for 90 days is given in Figure 143. From this figure it is seen that a small amount of platinum is present at the surface of the TZM to a depth of about $12\text{ }\mu\text{m}$. This platinum apparently was transported to the surface from the platinum and platinum-rhodium discs that were embedded in the fuel contained in these capsules. These were embedded to obtain information on more than one material at one time. The actual capsule design for these tests is given in Figure D-4. A sharp peak of titanium is observed approximately $38\text{ }\mu\text{m}$ from the surface, suggesting a small precipitate high in titanium. Photomicrographs of samples exposed for 90, 100, and 360 days are given in Figures 144-146, respectively. In general, these results are identical and reveal a small layer and precipitates near the surface which suggests some reaction. The precipitates are high in titanium. The depths of penetration of the titanium-bearing

particles are summarized in Table 14. The remainder of the reaction edge may be caused by the presence of platinum. No evidence of direct reaction with $^{238}\text{PuO}_2$ was found, and no plutonium was observed below the reaction interface.

1500°C Photomicrographs of samples of TZM exposed at 1500°C for 48, 96, 200, and 500 hr are shown in Figures 147-150, respectively. In these capsules it was impossible to retain the fuel in the capsule during polishing, except in the region between the plug and the sidewall. There seems to be very little indication of reaction except for the appearance of a few precipitates near the surface believed to be titanium-containing particles. The depth of penetration of these particles is summarized in Table 15. In the 500-hr sample, Figure 150, some evidence of mass transfer of molybdenum is seen. A few small fingers of molybdenum are shown extending into the region between the plug and the sidewall. Presumably this transfer mechanism is the same as that occurring with molybdenum. Samples exposed for 1000 and 2000 hr showed no apparent reaction except for the presence of the titanium-bearing particles.

1700°C A photomicrograph of a TZM sample exposed for 12 hr at 1700°C is shown in Figure 151. No obvious reaction is observed with the exception of small gray precipitates in the grain boundaries to a depth of about 130 μm . Photomicrographs of this sample taken with backscattered electrons and with the characteristic x-rays of titanium, molybdenum, chromium, iron, and cobalt are shown in Figures 152-157. Also, a trace of the electron microprobe strip chart analysis is given in Figure 158. From these figures it is obvious that concentration of chromium, iron, and cobalt is high near the reaction interface, tapering off to zero at about 150-175 μm from the interface. Superimposed upon the concentration curves is a curve showing the variation of microhardness as a function of distance from the interface. The correlation between microhardness and impurity concentration appears to be reasonably good. It can also be seen from these figures that the small dark gray particles contain titanium, chromium, and a small amount of zirconium.

A sample exposed for 24 hr is shown in Figure 159. This photomicrograph shows molybdenum surrounding some fuel particles between the plug and the sidewall. This sample is particularly puzzling because it is the only sample of TZM which showed this morphology. The sample suggests that either PuO_2 is attacking the TZM or that a mass transport phenomenon is taking place. A trace of the x-ray strip chart analysis is given in Figure 160. From this figure it is seen that the dark gray particles at the surface contain plutonium and chromium, and the molybdenum phase contains an appreciable amount of impurities. Also a small dark precipitate at a grain boundary contains titanium and chromium. Although it is not possible to determine whether mass transport or corrosion is responsible for this phenomenon, it should be emphasized that this is the only sample in which this observation was made.

A sample exposed for 500 hr, shown in Figure 161, is similar to that shown in Figure 151 except for the greater depth of penetration of the

titanium-bearing precipitates. Presumably these precipitates are the result of either chromium or oxygen, or both, forming a stable compound with titanium at the grain boundaries. A summary of the depths to which these precipitates are found for TZM at 1700°C is given in Table 16.

After exposure for 1000 hr the structure shown in Figure 162 was obtained. The fine-grained structure at the interface is rather unusual and at this point cannot be explained. The depth of penetration of iron into this sample was found to be about 950 μm , whereas chromium diffused about 650 μm into the surface. A microhardness traverse across the area microprobed is given in Figure 163. It is interesting to note that the microhardness values level off at about 950-1000 μm from the surface.

Discussion In general it can be said that no evidence of direct reaction between $^{238}\text{PuO}_2$ and TZM was observed. A small amount of mass transfer was observed, but the amount was considerably less than for pure molybdenum. It is quite possible that the presence of titanium and zirconium in the alloy inhibited the mass transfer considerably. If the formation of a molybdenum oxide is necessary for mass transfer to take place, titanium and zirconium could getter the oxygen in the system sufficiently to inhibit the formation of the molybdenum oxide. The presence of titanium and zirconium in precipitates in the grain boundaries lends some support to this concept.

Impurity penetration into the alloy was observed in TZM. A reasonable correlation between microhardness measurements and impurity concentration was found. In addition, it was observed that as the temperature of exposure increases the maximum hardness near the surface also increases. No data are available at 1200°C, but at 1500°C the microhardness values approach 600 VHN at the surface, and at 1700°C the microhardness values approach 1000 VHN for short-time tests. The microhardness at the interior of the alloy is 250-300 VHN. While the exact consequences of these impurities are unknown at this time, the high hardness values present the possibility of embrittlement of the surface. However, as Figure 163 suggests, longer exposure times even at 1700°C may result in a decrease in microhardness values near the surface.

MOLYBDENUM-50 WT % RHENIUM AT 1200°C

Photomicrographs of the reaction between $^{238}\text{PuO}_2$ and Mo-50 wt % Re after 60 and 180 days are shown in Figures 164 and 165. It is evident from these photomicrographs that considerable reaction has taken place. An x-ray strip chart analysis of the 180-day sample is shown in Figure 166. The appearance of this reaction zone is slightly different from that shown in Figure 165. This is the result of the fact that Figure 165 was taken along the side of the disc specimen, whereas Figure 166 was taken at the end of the specimen. The disc was punched out of a sheet of material which is responsible for the deformed structure at the edge. Figure 166 shows that no plutonium is present in the reaction layer. However, impurities from the fuel are present in significant amounts, particularly chromium, iron, nickel, and cobalt. This is also shown in

Figures 167-173 which are photomicrographs of the interface taken with backscattered electrons and characteristic x-rays. From these photomicrographs it is obvious that the distribution of these impurities is quite even across the sample. In Figure 170, however, cobalt is seen to be moving preferentially in the grain boundaries where the σ phase is found. Whether the higher rhenium concentration or the higher defect concentration of the boundary is responsible for this more rapid diffusion is not known at this time.

Microhardness measurements across this reaction zone for the 180-day sample are shown in Figure 174. The extremely high values near the surface suggest the formation of intermetallic compounds near the surface. A summary of the available binary phase diagrams of the impurity elements with molybdenum is given in Table 4.¹²⁻¹⁴ This table indicates that complex combinations of intermetallic compounds and solid solutions are possible. This is certainly verified in Figure 166.

Measurements of the width of the reaction layer for the various samples are summarized in Table 17. At 90 and 180 days, duplicate samples were available, and it is apparent that the agreement is poor.

Although no indications of direct reaction with PuO_2 were observed, it is obvious that impurities can exert an extremely deleterious effect on the reaction interface. Compound formation renders the interface quite brittle as indicated by microhardness measurements and the photomicrographs in Figures 164, 165, and 166, which show cracks in the compound layer normal to the interface. These cracks could serve as stress concentrators under service conditions.

RHENIUM

A photomicrograph and trace of the electron microprobe strip chart analysis of rhenium tested at 1500°C for 1000 hr is shown in Figure 175. This photomicrograph shows a uniform 10-12 μm wide, light-phase reaction zone in the metal along the fuel-rhenium interface. The electron microprobe strip chart analysis shows this region to contain tantalum of approximately constant composition.

The origin of the tantalum can be seen from the capsule design shown in Figure D-9. In this design a rhenium disc was embedded in the fuel which in turn was contained in a tantalum-10 wt % tungsten liner. Rhenium foil was placed between the fuel and the liner. This design was made necessary by the unavailability of rhenium tubing at the time these tests were started.

An estimate of the relative tantalum content in the reaction zone indicates that the zone contains 15-18 wt % tantalum. This suggests that this phase may be the χ phase of the Ta-Re binary system. According to Elliott¹³ the χ phase has a variable composition, and the limit of solubility on the rhenium side of this range may be between 12 and 20 wt % tantalum.

The mechanism of the transport of tantalum from the container material to the rhenium disc may be the vaporization of tantalum from the container material in the form of the volatile suboxide TaO_2 .³ Oxygen from the decomposition of the fuel apparently reacts with the container material to form Ta_2O_5 , which can then form TaO_2 (g) according to the reaction:

The TaO_2 could then react with the rhenium disc.

Due to the interference of the container material in this test, the compatibility specimen will be redesigned using rhenium tubing as the container material. It should be noted that tungsten from the container was not involved, nor was there any apparent reaction with the fuel or the impurities in the fuel.

TUNGSTEN

Tungsten compatibility studies were conducted at 1000, 1200, and 1500°C. Four specimen designs were used in these studies: 1) a tungsten crucible and plug machined from bar stock (1500°C), 2) a tungsten disc weld sealed inside a tantalum-10% wt tungsten capsule (1500°C), 3) a tungsten disc weld sealed inside a tungsten-26 wt % rhenium capsule (1200°C), and 4) a tungsten crucible made from seamless tubing and end caps made from sheet stock (1000°C). These capsule designs are shown in Figures D-6, D-8, D-5, and D-1 respectively. The inclusion of tantalum and rhenium in the tungsten/²³⁸PuO₂ study plus the presence of metallic impurities in the ²³⁸PuO₂ resulted in a very complex system for analysis.

It must be realized that the results of the compatibility study described in this section are not necessarily representative of a tungsten capsule containing pure ²³⁸PuO₂ isotopic fuel.

1000°C No reaction was detected after 532 days at 1000°C. A photomicrograph of the 532-day sample is shown in Figure 176.

1200°C The changes in dimension of the tungsten discs that were buried in ²³⁸PuO₂ are summarized in Table 18. The discs and fuel were contained in weld-sealed tungsten-26 wt % rhenium capsules, Figure D-5. Figures 177, 178, and 179 show the condition of these discs after 60 and 365 days at 1200°C. Microprobe traces of representative specimens are given in Figures 180, 181, and 182. These traces indicate that a thin (less than 10 μm) iron and chromium-rich layer is present on the surface. Less than 25 μm of the substrate were contaminated by the fuel impurities during the 60- and 90-day exposure of the analyzed specimens. It should be noted that these depths of penetration are not the true diffusion depths of iron and chromium for the given time periods. The original tungsten thickness continuously decreased during the thermal exposure. That is, the starting point (surface) for diffusion into the substrate had a certain mobility which continuously changed the distance coordinates of the diffusing elements.

The highly irregular surface of the tungsten discs shown in Figures 177 through 179 has also been observed by other investigators after testing at 2000°C.²² This phenomenon can be attributed to (1) preferred attack along the original columnar grain boundaries followed by separation of these grains from the substrate and (2) differences in attack rates of various crystallographic orientations of the tungsten (faceting).²³ Figure 183 shows the microstructure of the tungsten prior to testing. Note the regions of localized penetration along the grain boundaries of the columnar structure. This localized attack was caused by etching and the electrical discharge machining process, and serves to demonstrate the potentially heterogeneous corrosion that can occur with such a microstructure.

Figure 184 is a plot of the minimum and maximum amounts of surface recession for these tungsten specimens as a function of time at 1200°C. Also given in the figure is the oxidation behavior for pure tungsten at reduced oxygen pressures, as determined by Anderson²⁴ and Eisinger.²⁵ This apparent agreement between the observed corrosion behavior of the tungsten discs and the low-pressure oxidation of tungsten leads to the conjecture that the observed corrosion is a low pressure oxidation process. Unfortunately, the system is too complex to definitely establish a precise mechanism to explain the observed behavior. Some factors that should be considered are: 1) the equilibrium gas pressure for the reaction $2\text{Me} + \text{O}_2 \rightarrow 2\text{MeO}$ is between 10^{-5} to 10^{-7} torr for the oxides NiO, CoO, and FeO; 2) the quantity of these oxides in the sealed capsule that have high oxygen partial pressure is too small to sustain an oxidation reaction for more than one day; 3) a fraction of the metal impurities in the fuel could be present as ions dissolved in the $^{238}\text{PuO}_2$ and not as a free oxide; 4) continuous regeneration of FeO, CoO, and NiO would be difficult as the free energies of formation of these oxides are more positive than the free energies of formation of PuO_2 , Cr_2O_3 , and WO_3 ; 5) the gaseous oxides of rhenium from the tungsten-26 wt % rhenium are less stable than FeO, CoO, and NiO (Fe, Co, and Ni could reduce rhenium oxide to regenerate oxides of the desired oxygen partial pressure); 6) enrichment of the surface of the tungsten discs with iron and chromium would modify the tungsten oxidation process; 7) radiation from the $^{238}\text{PuO}_2$ would be expected to modify the reactions in the closed capsule system; and 8) other investigators²³ have observed attack of tungsten surfaces not in direct contact with $^{238}\text{PuO}_2$, thus suggesting a vapor/solid reaction. Metallic impurities of similar impurity levels used in this study were also used by the other investigators.

An examination of the tungsten-26 wt % rhenium compatibility results at 1200°C presents a probable mechanism for the continued regeneration of oxygen. The base of the tungsten-26 wt % rhenium capsules that contained these tungsten discs is covered with a pure tungsten deposit. This suggests that the tungsten oxide that formed at the disc surfaces is being reduced by a thermal deposition process at the base of the containers.

1500°C Figure 185 shows the appearance of a tungsten/ $^{238}\text{PuO}_2$ interface after completing 2000 hr (83.3 days) at 1500°C. This particular specimen

was the "crucible and plug" type design, shown in Figure D-6. Surface attack is visible in Figure 185. However, it is not the severe type seen at 1200°C. (The specimen design did not permit quantitative measurements to be made.)

The microprobe trace shown in Figure 185 identifies the dispersed particles in the fuel as tungsten. The spherical shape of these particles suggests that they were in contact with the fuel during the thermal exposure and are not metallographic artifacts produced during sectioning. (Diffusion and surface reaction tend to round off rough surfaces.) These tungsten particles were distributed uniformly throughout the $^{238}\text{PuO}_2$. The microprobe trace also identified a thin (less than 10 μm) surface layer on the tungsten substrate rich in the metallic fuel impurities chromium, iron, manganese, and cobalt. These elements were not detected below this surface layer.

Other tungsten specimens of this crucible and plug design were examined after shorter exposure times. The condition of these specimens was similar to the 2000-hr specimen.

Figure 186 shows the appearance of a tungsten disc that was buried in $^{238}\text{PuO}_2$ for 1000 hr (41.7 days) at 1500°C. The disc and fuel were weld-sealed inside a tantalum-10 wt % tungsten capsule during the test as shown in Figure D-8. A 40 μm thick oxide layer is present on the surface of the specimen. Figure 187 shows microprobe traces across the oxide layer into the substrate. Detection of tantalum in the oxide scale illustrates that the oxide is not merely the result of a tungsten and plutonium interaction. Figures 188 and 189 are photomicrographs of the reaction layer, taken with the characteristic tantalum and plutonium radiation. These figures further illustrate the presence of these elements in the oxide scale. The identification of tungsten in the oxide scale indicates that some material loss occurred during the 1000-hr exposure.

Metallic impurities present in the $^{238}\text{PuO}_2$ were not detected in the microprobe traces through the oxide or substrate. Figure 187 does indicate that some tantalum diffused into the tungsten disc to a depth of about 15 μm .

Metallographic measurement of the tungsten disc showed that the surface recession was negligible. No change in the dimensions of the disc were measured after the exposure within the error of the measurements ($\pm 15 \mu\text{m}$). This was the only disc specimen examined to date. Tungsten discs contained in $^{238}\text{PuO}_2$ -fueled tungsten containers are presently being tested to eliminate the side effects that occurred in the results discussed above.

Tungsten exhibited rather unusual behavior in these 1500°C tests. Corrosion was found to be much less at this temperature than at 1200°C. The presence of tantalum in the oxide scale of the tungsten discs tested at 1500°C and the presence of rhenium in the 1200°C test specimen assembly could have contributed to this apparent anomaly. Such differences in the chemistry of the two specimen assemblies tend to invalidate any meaningful analysis of the temperature variable. As pointed out earlier, the presence of tungsten-26 wt % rhenium in the system could have contributed to the instability of the tungsten discs.

Discussion The wrought structure of tungsten could contribute to the observed differences in behavior at 1200 and 1500°C. The wrought structure could be more sensitive to attack than a recrystallized structure due to orientation effects.²³ Tungsten starts to recrystallize at temperatures above 1400°C. Therefore, the 1500°C test specimens would develop an equiaxed grain structure after a few hours of testing.

Increasing the temperature from 1200 to 1500°C will increase the vapor pressure of the oxides. If the vapor species contains the oxygen molecule, oxidation of tungsten will occur. Oxidation will progress at a faster rate than at 1200°C as long as a source for oxygen is present. At 1500°C, the partial pressure of O₂ in equilibrium with ²³⁸PuO_{2.0} is about 10⁻¹ torr. As the ²³⁸PuO₂ loses oxygen the partial pressure of oxygen in equilibrium with the oxide rapidly decreases. For PuO_{1.92}, the oxygen partial pressure has decreased to 10⁻⁸ torr. Thus, even at the higher test temperature, oxygen is limited and must be regenerated to continue the oxidation of tungsten in a closed system.

TUNGSTEN-26 WT % RHENIUM

Three different capsule designs were used in the tungsten-26 wt % rhenium studies: 1) a tungsten-26 wt % rhenium crucible made from seamless tubing with end caps made from sheet stock (1000°C), 2) a tungsten-26 wt % rhenium capsule containing a tungsten disc embedded in the fuel (1200°C), and 3) a tungsten-26 wt % rhenium disc sealed inside a tantalum-10 wt % tungsten capsule (1500°C). These capsule designs are shown in Figures D-1, D-5, and D-8, respectively.

1000°C No reaction was detected for time periods up to 501 days at 1000°C. A photomicrograph of the 501-day sample is shown in Figure 190.

1200°C A photomicrograph of a tungsten-26 wt % rhenium sample exposed to ²³⁸PuO₂ for 60 days at 1200°C is shown in Figure 191. An intergranular reaction is shown, followed by a more continuous reaction layer at the interface. There appears to be no similarity between the intergranular reaction product and the continuous layer. Photomicrographs of this sample taken with backscattered electrons and the characteristic x-rays of cobalt, iron, tungsten, rhenium, and plutonium are shown in Figures 192-197. From these figures it can be seen that the intergranular reaction product contains fuel impurities cobalt and iron. An x-ray strip chart analysis also showed an increase in the rhenium content in the grain boundaries. The continuous layer at the reaction interface is shown to be primarily tungsten with no rhenium or impurities present.

A photomicrograph of a 90-day sample is shown in Figure 198 which shows a fuel particle partially surrounded by metal. A trace of the electron microprobe strip chart analysis is shown in Figure 199. The fuel particle is found to contain some chromium, iron, and cobalt. The region immediately adjacent to the particle is shown to be tungsten with no rhenium or impurities, whereas the thin band adjacent to the tungsten band contains an appreciable amount of impurities.

Further evidence of this phenomenon is shown in Figure 200 which shows a sample exposed for 365 days. Analysis with the electron microprobe gave the same distribution of elements shown in Figure 199. The thickness of the tungsten layer is approximately a linear function of time as shown in Figure 201. A reasonably linear plot of the data is obtained, with the exception of the 180-day data. However there is reason to believe that some loss of the surface occurred during sample preparation. Also included in this figure is the width of the intergranular penetration zone. Apparently the depth of intergranular penetration is independent of time.

The presence of tungsten at the reaction interface is somewhat disconcerting since it indicates an improper capsule design. The capsule design, shown in Figure D-5, was one in which a tungsten disc was embedded in the fuel which in turn was contained in the tungsten-26 wt % rhenium capsule. This design was necessitated by the unavailability of tungsten tubing at the time these tests were started. Apparently tungsten is transported, probably as an oxide, from the tungsten disc to the inside wall of the tungsten-26 wt % rhenium capsule. At this time it is not known why the tungsten deposited on the alloy in preference to any other site within the capsule.

The independence of the width of the intergranular penetration with respect to time, shown in Figure 201, suggests that the addition of tungsten to the surface inhibits any further reaction between the fuel and the alloy.

1500°C A photomicrograph of a sample tested for 1000 hr at 1500°C is shown in Figure 202. A line of precipitate particles is shown at a maximum depth of 12 μm from the surface. Electron microprobe analysis showed these particles to be high in rhenium, with no plutonium present, although plutonium was found at the edge of the sample. This sample was a disc embedded in fuel, which in turn was contained in a tantalum-10 wt % tungsten container. The corner of this disc is shown in Figure 203. The outside edge of the disc is shown with an apparently greater depth of penetration of these particles. Quantitative measurements should not be made on this edge, because the edge is not normal to the polished surface as is the side of the disc. However, this serves to magnify the reaction layer to the point where extensive porosity is shown at the interface. The presence of plutonium at the surface could very well be associated with the rhenium-rich phase (presumably rhenium oxide). No tantalum was observed at the interface although iron and chromium were found to depths of about 100 μm and 35 μm , respectively.

Discussion The presence of tungsten on the surface of the tungsten-26 wt % rhenium alloy at 1200°C in effect negates the validity of these tests as a test of the compatibility of the alloy with $^{238}\text{PuO}_2$. In order to obtain valid compatibility data, the tests should be duplicated with only tungsten-26 wt % rhenium in the system. However, the results suggest a rather interesting possibility for improving the compatibility of the alloy. If a heat source capsule were to be fabricated from tungsten-26 wt % rhenium alloy, the addition of a supply of tungsten inside of the capsule could result in the deposition of a layer of tungsten on the

inside of the capsule with a resultant improvement of the compatibility. Oxidation of tungsten probably occurs as a result of the free oxygen in the system which comes from the thermal decomposition of PuO_2 . Tungsten oxide is somewhat volatile at these temperatures and can migrate to a colder part of the capsule where it will decompose to tungsten metal plus oxygen.

HAFNIUM

Hafnium was tested, even though Table I suggests that it should reduce PuO_2 directly, because it is a constituent of T-111 and T-222. In lieu of hafnium tubing the capsule design, shown in Figure D-7, consisted of a hafnium disc embedded in fuel which in turn was contained in a tantalum-10 wt % tungsten container. Hafnium foil was placed between the fuel and the container.

A photomicrograph of hafnium tested at 1500°C for 1000 hr is shown in Figure 204. As shown in this photomicrograph, the 0.025 in. disc was completely degraded. When the disc was picked up for mounting for metallographic preparation, it broke into several pieces. A trace of the electron microprobe strip chart analysis is shown in Figure 205. The discontinuous layer at the top of the sample in Figure 204 is shown at the left side of Figure 205 (region 5). This layer contains a constant amount of plutonium and hafnium. Regions 3 and 4 consist of a dark-gray, slightly translucent, reaction product. The decrease in hafnium in regions 3 and 4 is rather unusual, in that a decrease is indicated in hafnium below that expected for the formation of HfO_2 , but no corresponding increase in any other element was found. This suggests that either a higher oxide form of hafnium is formed, the conductivity of the sample has changed with a resulting decrease in sensitivity, or the density of the sample has decreased in this area. The last two possibilities are most probable. No tantalum or tungsten from the container material was found. Further testing of hafnium has been discontinued.

ZIRCONIUM

Zirconium was tested with $^{238}\text{PuO}_2$ at 1700°C for 24, 48, 96, and 168 hr. Table I indicates that thermodynamically a reaction would be expected. However, in spite of this, these tests were conducted for two reasons. First, zirconium is a constituent of TZM, and second, there was the possibility that any reaction product would form a protective layer and inhibit any further reaction.

A photomicrograph of a zirconium control specimen is given in Figure 206. This figure shows the normal capsule configuration and void area normally occupied by the fuel. Figure 207 is a photomontage of a zirconium specimen after 168 hr at 1700°C and is typical of all the zirconium specimens tested at 1700°C . It is obvious from this figure that a gross reaction occurred between the fuel and container material. Unfortunately, the fuel and reaction products were lost during metallographic sectioning of the specimens making identification of the reaction products by x-ray analysis impossible. Electron microprobe analysis of the capsule shows

plutonium, iron, cobalt, and, to a lesser extent, chromium throughout the specimen grain boundaries to a depth in excess of 254 μm after 168 hr at 1700°C. Diffusion of these elements apparently occurs preferentially along the grain boundaries, although a general attack is also taking place. Reaction rates are impossible to determine from the data obtained.

Testing of this material has been discontinued at 1700°C and above. However, since test specimens have already been fabricated, tests will be conducted for shorter periods of time at lower temperatures in an attempt to determine a reaction rate and penetration depths. Special effort will be made to reclaim the reaction products for identification.

GENERAL DISCUSSION

From the data presented in this report it is obvious that each material reacts differently to $^{238}\text{PuO}_2$. In general, tantalum and tantalum alloys are similar in their behavior although there are important differences between them. Niobium reacts somewhat like tantalum which is not too surprising. Tantalum and tantalum alloys were found to absorb oxygen and become embrittled. At lower temperatures a surface layer of oxide as well as an intergranular oxide phase are formed, whereas at higher temperatures the amount of intergranular reaction product decreases.

Molybdenum and tungsten are similar in behavior which is also not unexpected. These metals suffer from a tendency toward mass transport of material from one part of the capsule to another. Molybdenum and molybdenum alloys also tend to develop hard, brittle, surface layers as a result of reaction with fuel impurities.

As a result of these differences, each of these materials has its own advantages and disadvantages. At the present time, any one material does not have overwhelming advantages over the other. Any advantage that one material has over the others on a compatibility basis must be balanced against other factors such as availability, cost, fabricability, etc.

During the course of this program it became obvious that the conclusions would be somewhat clouded, and that certain changes in test parameters could be made which might change the conclusions considerably. One of these changes would be to alter the purity of the fuel. As the test program progressed, the one problem that arose repeatedly was that of impurity elements at the reaction interface. Since production grade fuel, produced in accordance with SNAP-27 specifications, was used, it could contain as much as 2% nonactinide cation impurities. Reactions were found most frequently with the transition elements iron, chromium, nickel, cobalt, and manganese. The true effect of these elements on the compatibility of $^{238}\text{PuO}_2$ with the various metals is not known at this time. In some cases these elements could have a beneficial effect by strengthening the surface of the liner material or by actually inhibiting reactions with the fuel. Until definitive data on the true effects of the impurities have been obtained, it should not be assumed that the effects are either beneficial or deleterious.

In the case of molybdenum and molybdenum alloys, the impurities definitely seem to affect the surface adversely. This is particularly true of the molybdenum-50 wt % rhenium alloy. A hard and apparently brittle layer is formed at the interface in molybdenum alloys, and there are indications that the layer flakes off. However, with TZM there is also an indication that at long time exposures the diffusion of impurities extends far enough that the microhardness near the surface decreases. Apparently the limited supply of impurity elements tends to become distributed evenly throughout the TZM resulting in a decrease in concentration at the surface. If this effect is real, then for long time exposures the impurities are not necessarily deleterious.

For tantalum and tantalum alloys any hardness increase at the surface due to solution hardening from the cation impurities was masked by a hardness increase due to oxygen absorption. Probably one of the worst effects of the impurities is that they serve as an additional supply of oxygen because of their tendency to decompose at elevated temperatures. This extra oxygen would be especially deleterious to tantalum and tantalum alloys due to increased hardening effects.

The presence of the impurities casts some doubt on the ability of this work to determine the compatibility of pure $^{238}\text{PuO}_2$ with the various materials. The program is valuable to the extent that it shows the effects of production grade fuel on these materials.

There is no question that if the potential exists for a problem with the impurities, it is best to eliminate them if possible. As a result of the data generated during this work, steps are being taken to upgrade the production process in order to improve the purity of the production grade fuel. At the same time a program has also been initiated to determine the maximum amount of impurities that could be tolerated. These tests have been under way for some time, and when the results are accumulated a report will be written.

In the meantime, loading of new capsules with SNAP-27 grade fuel has been suspended. All new tests are being conducted with Savannah River Product (SRP) fuel containing approximately 2600 ppm total cation impurities. In addition, some of the work discussed in this report is being duplicated using SRP fuel.

The mechanism of the mass transport phenomenon observed with molybdenum and tungsten is not known at this time. It appears to be a complex reaction involving oxygen. This phenomenon may have serious implications in actual service because of eventual uneven distribution of mass by the preferential loss of material in one region and buildup in another, and because of the potential for plugging the venting device. Until the exact nature of this mass transport effect is understood, its exact effects on a heat source capsule are difficult to predict.

This work has shown that careful attention to the design of compatibility capsules is absolutely necessary. Capsule design must be dictated by

either of two criteria which are mutually exclusive. The first criterion is that the compatibility test is to determine only the reaction between two materials in contact with each other. In this case all other materials must be kept out of the system and the components must be as pure as possible to avoid side reactions. A second criterion is that the compatibility test is to simulate actual operating conditions as much as possible. Some of the variables in this situation are; time, temperature, environment (atmosphere, vacuum, etc.), fuel purity, number and type of components in the system, pressure, fuel weight/liner weight ratio, and surface area/volume ratio.

In these tests, neither of these two criteria were fully satisfied. In view of the fact that production grade fuel was used in all of these tests the first criterion was not met. As a result most of the work could be described as satisfying the second one, if actual heat source capsules will have only one material within the fuel enclosure. However, when two or more materials were tested in the same capsule not even the second criterion was satisfied. When the capsule material is the same as the disc embedded in the fuel, the second criterion can be satisfied except when the design of an actual heat source capsule is such that more than one material will be used in the interior of the capsule. In this case tests should be run using only these materials.

Applications and Implications of the Data The data presented in this report hold considerable significance for the radioisotopic heat source program. In this section, an attempt will be made to discuss the implications of the data and their application to the overall heat source problem.

Early in the program, data obtained on tantalum and tantalum alloys, suggested that free oxygen from the decomposition of PuO_2 to PuO_{2-x} was responsible for the oxidation of these alloys. The more recent data presented in this report tend to confirm this. These observations suggest that if substoichiometric fuel PuO_{2-x} were used instead of stoichiometric PuO_2 , the amount of free oxygen would be decreased to a very low level which would in turn inhibit the oxidation of the tantalum. Thermodynamic calculations for tantalum suggested that $\text{PuO}_{1.80}$ would be optimum. As a result of these calculations, samples of $\text{PuO}_{1.80}$ were produced at Mound Laboratory and sent to Donald W. Douglas Laboratories for testing at 1800°C . Recent data on tungsten, tungsten-20 wt % rhenium, and rhenium indicate a significant improvement of $\text{PuO}_{1.80}$ over $\text{PuO}_{2.0}$.²³

In the case of molybdenum, the difference in the mass transport effects in molybdenum compared to TZM also suggest that the presence of oxygen is necessary for this phenomenon, although the exact mechanism is not known at this time. A mass transport phenomenon is also observed with tungsten when tested with PuO_2 , but not with $\text{PuO}_{1.8}$.²³ All of these observations suggest that a substoichiometric fuel, or at least a means of removing the oxygen from the system, is both desirable and may even be necessary in some cases.

Several different techniques are possible as an alternative to PuO_{2-x} . The first technique involves the use of a gettering agent mixed in with the fuel. Tantalum or yttrium powder could be intimately mixed with the fuel where it could getter most of the free oxygen in the system before it had an opportunity to react with the liner material. A second technique is to either (1) make a thicker walled tantalum alloy capsule so that it can absorb enough oxygen interstitially that the rate of formation of Ta_2O_5 will be kept to a minimum or (2) add massive pieces of tantalum in the interior of the capsule to act as a "sponge" for the free oxygen thereby decreasing the partial pressure of free oxygen. These two alternatives would be best when PuO_2 powder, microspheres, or wafers are used as the fuel form. A third technique, useful with a cermet fuel form with a metal matrix, is to add Ta, Nb, Ti, etc. to the matrix material to react preferentially with the oxygen and in effect produce PuO_{2-x} .

When tantalum or tantalum alloys absorb oxygen they become embrittled. This is indicated particularly by the 1200°C data in which some of the samples shattered when handled. A brittle liner cannot deform without cracking. Therefore, a brittle liner cannot be expected to remain intact after impact. Even though a liner is not expected to carry any load, the small extra margin of safety afforded by a ductile liner could well be worth some extra effort to retain the original ductility of the material.

Mass transport of molybdenum and tungsten inside a heat source capsule could have serious implications, particularly in vented systems. Until the mechanism is properly understood, control of the movement of material inside the capsule is difficult. In a vented system, the transport of mass could plug the vent, thereby rendering it useless.

The data presented on tungsten and tungsten-26 wt % rhenium at 1200°C suggest a method of improving the compatibility of $^{238}\text{PuO}_2$ with the tungsten-26 wt % rhenium alloy. In these tests a tungsten disc was embedded in the fuel which in turn was welded into a tungsten-26 wt % rhenium capsule. Severe attack of the tungsten disc was observed and tungsten was found as a layer on the surface of the alloy. Because of this protective layer, the alloy was unaffected by the fuel. If tungsten-26 wt % rhenium were to be used for a heat source capsule, the compatibility may be improved by the use of tungsten within the capsule and by controlling the thermal condition so that the inside of the liner would become coated with a layer of tungsten.

CONCLUSIONS

From the data presented, it is apparent that quantitative data and their application to heat source capsules are dependent upon the design of the experiments. All the capsules used in this work were sealed capsules. Data are not available on the applicability of these data to a vented heat source capsule design. Non-selective vents in which the oxygen could be removed to a vacuum, could be desirable in some cases. The amount of PuO_2 in each capsule was less than 2 g so that the supply of oxygen from the fuel would be more limited than in a capsule with a larger fuel volume/surface area ratio.

The Group IVB metals, hafnium and zirconium, proved to be incompatible with $^{238}\text{PuO}_2$ as expected from thermodynamic considerations. Work has been terminated on these materials.

The Group VB metals, tantalum and niobium, reacted differently to $^{238}\text{PuO}_2$ than did the Group VIB metals, molybdenum and tungsten. Solution of oxygen in the Group VB metals, as well as diffusion of metallic impurities from the fuel, increase the container hardness. Embrittlement of these metals was observed. Hardness increases in the Group VIB metals and alloys are attributed to metallic impurities from the fuel. The depth of penetration of these impurities was correlated reasonably well with changes in microhardness. Surface oxide products and intergranular oxidation are more prevalent with the Group VB metals than with the Group VIB metals.

Tantalum, molybdenum, tungsten, and their alloys are, in general, effective barriers to plutonium at temperatures of 1500°C and lower. Plutonium was identified only in the surface reaction products after exposure at 1000 , 1200 , and 1500°C . Plutonium was observed in grain boundaries and precipitates in the container materials at temperatures of 1700°C and above. The compatibility of the alloys of the Group VB and VIB metals was in general similar to that of their respective pure metals, although in some instances differences were noted. This is shown by the comparison between tantalum-10 wt % tungsten and tantalum.

Arrhenius plots were difficult to obtain. Some of this difficulty results from scatter in the available data. However, some of the difficulty seems to be the result of changes in mechanism with increasing temperatures. Corrosion of tantalum, for example, changes from an intergranular mode of attack at 1000°C to a uniform attack at 1200 and 1500°C , to apparent pipe diffusion along grain edges at 1700°C . Under these circumstances a non-linear Arrhenius plot would be expected.

Corrosion of container materials occurs primarily where the fuel contacts the container walls in the partially filled capsules tested at 1000 and 1200°C . However, solid/solid interdiffusion is not the only reaction mechanism. Evidence of vapor transport was observed in several systems, particularly tungsten and molybdenum. The possibility of vapor transport suggests a potential problem for vented capsule designs. Further work should be done to establish the mechanism in order to minimize the problem.

Metallic impurities from the fuel, such as iron, cobalt, nickel, and manganese contribute to fuel/container interactions and complicate the interpretation of the results. The true effect of these impurities is unknown, although for molybdenum and tungsten the formation of a brittle surface reaction product is apparent.

Complex interactions can occur when more than one type of material is placed in contact with PuO_2 . Test capsule designs should be such that only one material is present within the system. When more than one material is to be present in an actual heat source capsule, tests should be

run on these materials in combination with each other. Mass transport of tungsten onto a tungsten-26 wt % rhenium container is an example of the situations which can arise.

Thermal decomposition of PuO_2 and thermodynamic considerations suggest that substoichiometric fuel is desirable. The results presented in this report tend to confirm this. Several suggestions have been put forward on ways to achieve substoichiometry inside the capsule.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the contributions of many people at Mound Laboratory. Mr. K. L. Breakall and Mr. R. E. Fitzharris performed most of the metallography, and Mr. D. L. Roesch performed all of the electron microprobe analyses. In addition, Dr. B. R. Kokenge contributed greatly to the thermodynamic interpretations used in this report.

REFERENCES

1. J. E. Selle, J. R. McDougal, and D. R. Schaeffer, The Compatibility of $^{238}\text{PuO}_2$ with Platinum and Platinum-Rhodium Alloys - Interim Report, MLM-1684, (December 31, 1969), 124 pp.
2. O. Kubaschewski and H. Speidel, J. Inst. Metals, 75, 417 (1948-49).
3. C. B. Alcock, Chemistry in Britain, 5:5, 216 (1969).
4. A. Glassner, The Thermochemical Properties of the Oxides, Fluorides, and Chlorides to 2500°K, ANL-5750, Argonne National Laboratory, Argonne, Illinois (October 1965).
5. F. L. Oetting, Chem. Rev., 67:3, 261 (1967).
6. R. J. Ackermann, R. L. Faircloth and M. H. Rand, J. Phys. Chem., 70:11, 3698 (1966).
7. The Plutonium-Oxygen and Uranium-Plutonium-Oxygen System: A Thermochemical Assessment, report of a panel on Thermodynamics of Plutonium Oxides held in Vienna, October 24-25, 1966, International Atomic Energy Agency, Vienna (1967).
8. W. L. Worrell, Measurements of the Thermodynamic Stabilities of the Niobium and Tantalum Oxides Using a High Temperature Galvanic Cell, UCRL-11957, Lawrence Radiation Laboratory, Livermore, Calif., (June 1965).
9. J. M. Criscione, R. A. Mercuri, E. P. Schram, A. W. Smith, and H. F. Volk, High Temperature Protective Coatings for Graphite, ML-TDR-64-173, Union Carbide Corporation, Carbon Products Division, Parma, Ohio (June 1964).
10. A. N. Nesmeyanov, Vapor Pressure of the Chemical Elements, Robert Gary (ed.), Elsevier Publishing Company, New York, N. Y., 1963.
11. J. E. Selle, A Summary of the Phase Diagrams and Compatibility of PuO_2 with Various Materials, MLM-1589 (April 25, 1969).
12. M. Hansen and K. Anderko, Constitution of Binary Alloys, 2nd Ed., McGraw-Hill Book Company, New York, N. Y., 1958.

13. R. P. Elliott, Constitution of Binary Alloys, First Supplement, McGraw-Hill Book Company, New York, N. Y., 1965.
14. F. A. Shunk, Constitution of Binary Alloys, Second Supplement, McGraw-Hill Book Company, New York, N. Y., 1969.
15. N. L. Peterson, Diffusion in Refractory Metals, WADD-TR-60-793, Wright Air Development Division, Wright-Patterson Air Force Base, Ohio (March 1961).
16. J. Askill, A Bibliography on Tracer Diffusion in Metals - Part III Self and Impurity Diffusion in Alloys, ORNL-3795, Oak Ridge National Laboratory, Oak Ridge, Tennessee (February 1967).
17. P. Kofstad, High Temperature Oxidation of Metals, John Wiley and Sons, New York, N. Y., 1966, pp. 164-165.
18. W. Batey, J. I. Bramman, H. W. Irons, and G. Yates, J. Nucl. Mater., 29, 229 (1969).
19. P. Kofstad, J. Less-Common Metals, 5, 158 (1963).
20. C. R. Tottle, J. Inst. Metals, 85, 377 (1957).
21. C. J. Smithells, Metals Reference Book, Volume I, 4th Ed., Plenum Press, New York, N. Y., 1967, p. 229.
22. R. A. Perkins, W. L. Price and D. D. Crooks, Oxidation of Tungsten at Ultra-High Temperatures, Tech. Report 6-90-62-98, Lockheed Missiles and Space Co., (1962).
23. R. L. Andelin and J. D. Watrous, Plutonia/Compatibility Testing, Quarterly Report No. 3, April-June 1969, DAC-63372, Donald W. Douglas Laboratories, Richland, Washington (July 1969).
24. H. Anderson, Ph.D Thesis, University of California, Lawrence Radiation Laboratory, April 1962.
25. J. Eisinger, J. Chem. Phys., 30, 412 (1959).

FIGURE 1 - Relative electron microprobe displacements for tungsten in a tantalum-10 wt % tungsten alloy at three different counting rates.

FIGURE 3 - Vapor pressures of selected elements as a function of reciprocal temperature.

FIGURE 4 - Diffusion coefficients for oxygen in tantalum,¹⁵ niobium,¹⁵ zirconium,¹⁷ and hafnium.¹⁷

FIGURE 5 - Photomicrograph of reaction between $^{238}\text{PuO}_2$ micro-spheres and tantalum after 516 days at 1000°C . (145X)

FIGURE 6 - Photomicrograph of reaction between $^{238}\text{PuO}_2$ micro-spheres and tantalum after 516 days at 1000°C . (555X)

FIGURE 7 - Penetration rate curves for tantalum and SGS tantalum in contact with $^{238}\text{PuO}_2$ microspheres at 1000°C .

FIGURE 8 - Electron backscatter photomicrograph of reaction layer in tantalum. (440X)

FIGURE 9 - X-ray emission picture of reaction layer in tantalum; tantalum $L\alpha$ radiation. (440X)

FIGURE 10 - Photomicrograph of base of tantalum capsule after 60 days at 1200°C. (53.4X)

FIGURE 11 - Photomicrograph of base of tantalum capsule after 92 days at 1200°C. (53.4X)

FIGURE 12 - Photomicrograph of base of tantalum capsule after 180 days at 1200°C. (53.4X)

FIGURE 13 - Photomicrograph of reaction layer on tantalum after 92 days at 1200°C. (512X)

FIGURE 14 - Photomicrograph of reaction layer on tantalum after 180 days at 1200°C. (512X)

FIGURE 15 - Trace of the electron microprobe strip chart analysis of tantalum after 92 days at 1200°C.

FIGURE 16 - Trace of the electron microprobe strip chart analysis of tantalum after 180 days at 1200°C.

FIGURE 17 - Photomicrograph of reaction interface of tantalum after 48 hr at 1500°C. (250X)

FIGURE 18 - Photomicrograph of reaction interface of tantalum after 168 hr at 1500°C. (100X)

FIGURE 19 - Photomicrograph of tantalum after 168 hr at 1500°C, taken with backscattered electrons. (220X)

FIGURE 20 - Photomicrograph of tantalum after 168 hr at 1500°C, taken with tantalum $L\alpha$ radiation. (220X)

FIGURE 21 - Photomicrograph of tantalum after 168 hr at 1500°C, taken with plutonium $M\alpha$ radiation. (220X)

FIGURE 22 - Photomicrograph of tantalum after 168 hr at 1500°C, taken with chromium $K\alpha$ radiation. (220X)

FIGURE 23 - Photomicrograph of tantalum after 168 hr at 1500°C, taken with iron $K\alpha$ radiation. (220X)

FIGURE 24 - Photomicrograph of tantalum after 168 hr at 1500°C, taken with cobalt $K\alpha$ radiation.

FIGURE 25 - Photomicrograph of tantalum disc after 1000 hr at 1500°C. (58.2X)

FIGURE 26 - Microhardness of a tantalum disc after 1000 hr at 1500°C.

FIGURE 27 - Photomicrograph of tantalum after 168 hr at 1700°C.
(120X)

FIGURE 28 - Photomicrograph
of tantalum after 500 hr at
1700°C. (23X)

FIGURE 29 - Trace of the electron microprobe strip chart analysis of tantalum after 200 hr at 1700°C.

FIGURE 30 - Trace of the electron microprobe strip chart analysis of tantalum after 500 hr at 1700°C.

FIGURE 31 - Microhardness traverse on tantalum after 500 hr at 1700°C, along with electron microprobe traverse.

Basis: Tantalum Tubing Filled with $\text{PuO}_{2.00}$ of a Bulk Density of 6.9 g/cm^3 .
 Fuel Contains 0.5 wt % Metal Impurities as MeO .

FIGURE 32 - Potential for tantalum oxidation as a function of container diameter.

FIGURE 33 - Photomicrograph of reaction between tantalum-10 wt % tungsten and $^{238}\text{PuO}_2$ microspheres after 516 days at 1000°C . (555X)

FIGURE 34 - Penetration rate curve for tantalum-10 wt % tungsten at 1000°C .

FIGURE 35 - Photomicrograph of base of tantalum-10 wt % tungsten capsule after 360 days at 1200°C. (53.4X)

FIGURE 36 - Photomicrograph of duplicate sample of tantalum-10 wt % tungsten after 360 days at 1200°C. (53.4X)

FIGURE 37 - Trace of the electron microprobe strip chart analysis of tantalum-10 wt % tungsten after 360 days at 1200°C .

FIGURE 38 - Photomicrograph of tantalum-10 wt % tungsten after 360 days at 1200°C, taken with backscattered electrons. (880X)

FIGURE 39 - Photomicrograph of tantalum-10 wt % tungsten after 360 days at 1200°C, taken with plutonium $M\alpha$ radiation. (880X)

FIGURE 40 - Photomicrograph of tantalum-10 wt % tungsten after 360 days at 1200°C, taken with tantalum $L\alpha$ radiation. (880X)

FIGURE 41 - Photomicrograph of tantalum-10 wt % tungsten after 360 days at 1200°C, taken with tungsten $L\alpha$ radiation. (880X)

FIGURE 42 - Photomicrograph of tantalum-10 wt % tungsten after 360 days at 1200°C, taken with chromium K α radiation. (880X)

FIGURE 43 - Photomicrograph of tantalum-10 wt % tungsten after 360 days at 1200°C, taken with iron K α radiation. (880X)

FIGURE 44 - Photomicrograph of duplicate sample of tantalum-10 wt % tungsten after 360 days at 1200°C. (512X)

FIGURE 45 - Trace of the electron microprobe strip chart analysis of tantalum-10 wt % tungsten after 120 days at 1200°C, using fuel containing 0.27% iron and 0.26% chromium.

FIGURE 46 - Photomicrograph of tantalum-10 wt % tungsten after 120 days at 1200°C, using fuel containing 0.27% iron and 0.26% chromium. (560X)

FIGURE 47 - Photomicrograph of tantalum-10 wt % tungsten after 120 days at 1200°C, using fuel containing 0.05% iron and 0.05% chromium. (109X)

FIGURE 48 - Photomicrograph of tantalum-10 wt % tungsten after 60 days at 1200°C, using fuel containing 0.15% iron and 0.15% chromium. (109X)

FIGURE 49 - Photomicrograph of the external edge of the base of a tantalum-10 wt % tungsten capsule after 30 days at 1200°C, showing diffusion and localized oxidation. (500X)

FIGURE 50 - Trace of the electron microprobe strip chart analysis of tantalum-10 wt % tungsten after 96 hr at 1500°C.

FIGURE 51 - Trace of the electron microprobe strip chart analysis of tantalum-10 wt % tungsten after 200 hr at 1500°C.

FIGURE 52 - Microhardness traverses on tantalum-10 wt % tungsten after contact with $^{238}\text{PuO}_2$ powder at 1500°C.

FIGURE 53 - Photomicrograph of tantalum-10 wt % tungsten after 48 hr at 1700°C. (100X)

FIGURE 54 - Trace of the electron microprobe strip chart analysis of tantalum-10 wt % tungsten after 1000 hr at 1700°C.

FIGURE 55 - Photomicrograph of tantalum-10 wt % tungsten after 1000 hr at 1700°C, taken with plutonium $M\alpha$ radiation. (220X)

FIGURE 56 - Photomicrograph of tantalum-10 wt % tungsten after 1000 hr at 1700°C, taken with tantalum $L\alpha$ radiation. (220X)

FIGURE 57 - Photomicrograph of tantalum-10 wt % tungsten after 1000 hr at 1700°C, taken with tungsten $L\alpha$ radiation. (220X)

FIGURE 58 - Photomicrograph of tantalum-10 wt % tungsten after 1000 hr at 1700°C, taken with iron $K\alpha$ radiation. (220X)

FIGURE 59 - Photomicrograph of tantalum-10 wt % tungsten after 1000 hr at 1700°C, taken with cobalt K α radiation. (220X)

FIGURE 60 - Photomicrograph of tantalum-10 wt % tungsten after 1000 hr at 1700°C, showing intergranular penetration of plutonium-bearing phase and metallic particles in the fuel. (69X)

FIGURE 61 - Schematic of test capsule for 2500°C test.

FIGURE 62 - Photomontage of tantalum-10 wt % tungsten after 5 min at 2500°C.

FIGURE 63 - Trace of electron microprobe strip chart analysis of tantalum-10 wt % tungsten after 5 min at 2500°C.

FIGURE 64 - Photomicrograph of reaction with T-222 alloy after 532 days at 1000°C. (555X)

FIGURE 65 - Reaction rate curve for T-222 in contact with $^{238}\text{PuO}_2$ microspheres at 1000°C .

FIGURE 66 - Photomicrograph of T-222 after 60 days at 1200°C . (106X)

FIGURE 67 - Photomicrograph of T-222 after 90 days at 1200°C.
(106X)

FIGURE 68 - Reaction rate curves for T-222 in contact with $^{233}\text{PuO}_2$ powder at 1200°C .

FIGURE 69 - Trace of the electron microprobe strip chart analysis of T-222 after 90 days at 1200°C .

FIGURE 70 - Trace of the electron microprobe strip chart analysis of T-222 after 180 days at 1200°C.

FIGURE 71 - Trace of the electron microprobe strip chart analysis of T-222 after 180 days at 1200°C .

FIGURE 72 - Photomicrograph of T-111 after 24 hr at 1700°C.
(250X)

FIGURE 73 - Trace of the electron microprobe strip chart analysis of T-111 after 48 hr at 1700°C.

FIGURE 74 - Trace of the electron microprobe strip chart analysis of T-111 after 500 hr at 1700°C.

FIGURE 75 - Reaction rate curve for T-111 in contact with $^{238}\text{PuO}_2$ powder at 1700°C .

FIGURE 76 - Reaction rate as a function of reciprocal temperature for T-111 (222) alloy.

FIGURE 77 - Photomicrograph of niobium after 12 hr at 1500°C.
(250X)

FIGURE 78 - Photomicrograph of niobium after 24 hr at 1500°C.
(250X)

FIGURE 79 - Photomicrograph of niobium after 24 hr at 1500°C, taken with backscattered electrons. (440X)

FIGURE 80 - Photomicrograph of niobium after 24 hr at 1500°C, taken with plutonium $M\alpha$ radiation. (440X)

FIGURE 81 - Photomicrograph of niobium after 96 hr at 1500°C. (250X)

FIGURE 82 - Microhardness traverse of niobium after 375 hr at 1500°C.

FIGURE 83 - Reaction rate curve for niobium as determined by microhardness measurements after 1500°C exposure.

FIGURE 84 - Minimum microhardness values for niobium as a function of $t^{1/2}$, after 1500°C exposure.

FIGURE 85 - Photomicrograph of niobium after 24 hr at 1700°C.
(135X)

FIGURE 86 - Trace of the electron microprobe strip chart analysis of niobium after 24 hr at 1700°C.

FIGURE 87 - Photomicrograph of niobium after 168 hr at 1700°C.
(120X)

FIGURE 88 - Photomicrograph of molybdenum after 60 days at 1200°C.
(360X)

FIGURE 89 - Photomicrograph of molybdenum after 60 days at 1200°C, taken with backscattered electrons. (1760X)

FIGURE 90 - Photomicrograph of molybdenum after 60 days at 1200°C, taken with iron $K\alpha$ radiation. (1760X)

FIGURE 91 - Photomicrograph of molybdenum after 60 days at 1200°C, taken with cobalt $K\alpha$ radiation. (1760X)

FIGURE 92 - Photomicrograph of molybdenum after 60 days at 1200°C, taken with plutonium $M\alpha$ radiation. (1760X)

FIGURE 93 - Photomicrograph of molybdenum after 60 days at 1200°C, taken with molybdenum $L\alpha$ radiation (1760X)

FIGURE 94 - Trace of the electron microprobe strip chart analysis of molybdenum after 60 days at 1200°C.

FIGURE 95 - Photomicrograph of molybdenum after 180 days at 1200°C. (250X)

FIGURE 96 - Photomicrograph of molybdenum after 180 days at 1200°C. (250X)

FIGURE 97 - Photomicrograph of molybdenum after 180 days at 1200°C, taken with backscattered electrons. (440X)

FIGURE 98 - Photomicrograph of molybdenum after 180 days at 1200°C, taken with molybdenum L α radiation. (440X)

FIGURE 99 - Photomicrograph of molybdenum after 180 days at 1200°C, taken with plutonium $M\alpha$ radiation. (440X)

FIGURE 100 - Photomicrograph of molybdenum after 180 days at 1200°C, taken with cobalt $K\alpha$ radiation. (440X)

FIGURE 101 - Photomicrograph of molybdenum after 180 days at 1200°C, taken with iron $K\alpha$ radiation. (440X)

FIGURE 102 - Photomicrograph of molybdenum after 180 days at 1200°C, taken with chromium $K\alpha$ radiation. (440X)

FIGURE 103 - Trace of the electron microprobe strip chart analysis and microhardness traverse of molybdenum after 180 days at 1200°C.

FIGURE 104 - Photomicrograph of molybdenum after 48 hr at 1500°C.
(100X)

FIGURE 105 - Photomicrograph of molybdenum after 200 hr at 1500°C.
(100X)

FIGURE 106 - Trace of the electron microprobe strip chart analysis of molybdenum after 200 hr at 1500°C.

FIGURE 107 - Photomicrograph of molybdenum after 500 hr at 1500°C.
(100X)

FIGURE 108 - Trace of the electron microprobe strip chart analysis of molybdenum after 1000 hr at 1500°C.

FIGURE 109 - Photomicrograph of molybdenum after 12 hr at 1700°C.
(250X)

FIGURE 110 - Photomicrograph of molybdenum after 24 hr at 1700°C.
(135X)

FIGURE 111 - Photomicrograph of molybdenum after 96 hr at 1700°C.
(250X)

FIGURE 112 - Photomicrograph of molybdenum after 200 hr at 1700°C.
(135X)

FIGURE 113 - Trace of the electron microprobe strip chart analysis of molybdenum after 96 hr at 1700°C .

FIGURE 114 - Photomicrograph of molybdenum after 96 hr at 1700°C, taken with backscattered electrons. (880X)

FIGURE 115 - Photomicrograph of molybdenum after 96 hr at 1700°C, taken with chromium K α radiation. (880X)

FIGURE 116 - Photomicrograph of molybdenum after 96 hr at 1700°C, taken with manganese $K\alpha$ radiation. (880X)

FIGURE 117 - Photomicrograph of molybdenum after 96 hr at 1700°C, taken with iron $K\alpha$ radiation. (880X)

FIGURE 118 - Photomicrograph of molybdenum after 96 hr at 1700°C, taken with cobalt $K\alpha$ radiation. (880X)

FIGURE 119 - Photomicrograph of molybdenum after 96 hr at 1700°C, taken with silicon $K\alpha$ radiation. (880X)

FIGURE 120 - Photomicrograph of molybdenum after 96 hr at 1700°C, taken with molybdenum $L\alpha$ radiation. (880X)

FIGURE 121 - Photomicrograph of molybdenum after 96 hr at 1700°C, taken with plutonium $M\alpha$ radiation. (880X)

FIGURE 122 - Photomicrograph of molybdenum after 500 hr at 1700°C.
(250X)

FIGURE 123 - Photomicrograph of molybdenum after 1000 hr at 1700°C.
(250X)

FIGURE 124 - Photomicrograph of molybdenum after 1000 hr at 1700°C, taken with backscattered electrons. (440X)

FIGURE 125 - Photomicrograph of molybdenum after 1000 hr at 1700°C, taken with sample current. (440X)

FIGURE 126 - Photomicrograph of molybdenum after 1000 hr at 1700°C, taken with plutonium M α radiation. (440X)

FIGURE 127 - Photomicrograph of fuel contained in molybdenum for 25 hr at 1900°C. (150X)

FIGURE 128 - Photomicrograph of fuel contained in molybdenum for 25 hr at 1900°C. (296X)

FIGURE 129 - Photomicrograph of fuel contained in molybdenum for 25 hr at 1900°C, taken with backscattered electrons. (880X)

FIGURE 130 - Photomicrograph of fuel contained in molybdenum for 25 hr at 1900°C, taken with chromium K α radiation. (880X)

FIGURE 131 - Photomicrograph of fuel contained in molybdenum for 25 hr at 1900°C, taken with silicon K α radiation. (880X)

FIGURE 132 - Photomicrograph of fuel contained in molybdenum for 25 hr at 1900°C, taken with plutonium $M\alpha$ radiation. (880X)

FIGURE 133 - Photomicrograph of molybdenum after 25 hr at 1900°C. (296X)

FIGURE 134 - Photomicrograph of molybdenum after 500 hr at 1900°C.
(226X)

FIGURE 135 - Microhardness values and impurity concentration as a function of distance from the reaction interface on molybdenum tested 200 hr at 1700°C.

FIGURE 136 - Photomicrograph of TZM after 32 days at 1200°C.
(250X)

FIGURE 137 - Photomicrograph of TZM after 62 days at 1200°C.
(250X)

FIGURE 138 - Photomicrograph of TZM after 62 days at 1200°C,
taken with backscattered electrons. (440X)

FIGURE 139 - Photomicrograph of TZM after 62 days at 1200°C,
taken with plutonium $M\alpha$ radiation. (440X)

FIGURE 140 - Photomicrograph of TzM after 62 days at 1200°C,
taken with titanium $K\alpha$ radiation. (440X)

FIGURE 141 - Photomicrograph of TzM after 62 days at 1200°C,
taken with molybdenum $L\alpha$ radiation. (440X)

FIGURE 142 - Photomicrograph of TZM after 62 days at 1200°C,
taken with chromium K α radiation. (440X)

FIGURE 143 - Trace of the electron microprobe strip chart analysis of TZM after 90 days at 1200°C.

FIGURE 144 - Photomicrograph of TZM after 90 days at 1200°C.
(250X)

FIGURE 145 - Photomicrograph of TZM after 180 days at 1200°C.
(250X)

FIGURE 146 - Photomicrograph of TzM after 360 days at 1200°C.
(250X)

FIGURE 147 - Photomicrograph of TzM after 48 hr at 1500°C.
(250X)

FIGURE 148 - Photomicrograph of TZM after 96 hr at 1500°C.
(100X)

FIGURE 149 - Photomicrograph of TZM after 200 hr at 1500°C.
(100X)

FIGURE 150 - Photomicrograph of TzM after 500 hr at 1500°C.
(250X)

FIGURE 151 - Photomicrograph of TzM after 12 hr at 1700°C.
(195X)

FIGURE 152 - Photomicrograph of TZM after 12 hr at 1700°C, taken with backscattered electrons. (440X)

FIGURE 153 - Photomicrograph of TZM after 12 hr at 1700°C, taken with titanium K α radiation. (440X)

FIGURE 154 - Photomicrograph of TZM after 12 hr at 1700°C, taken with molybdenum $L\alpha$ radiation. (440X)

FIGURE 155 - Photomicrograph of TZM after 12 hr at 1700°C, taken with chromium $K\alpha$ radiation. (440X)

FIGURE 156 - Photomicrograph of TzM after 12 hr at 1700°C, taken with iron $K\alpha$ radiation. (440X)

FIGURE 157 - Photomicrograph of TzM after 12 hr at 1700°C, taken with cobalt $K\alpha$ radiation. (440X)

FIGURE 158 - Trace of the electron microprobe strip chart analysis and microhardness traverse of TZM after 12 hr at 1700°C.

FIGURE 159 - Photomicrograph of TZM after 24 hr at 1700°C.
(135X)

FIGURE 160 - Trace of the electron microprobe strip chart analysis of TZM after 24 hr at 1700°C.

FIGURE 161 - Photomicrograph of TZM after 500 hr at 1700°C.
(135X)

FIGURE 162 - Photomicrograph of TZM after 1000 hr at 1700°C.
(58X) (Etched)

FIGURE 163 - Microhardness traverse across TZM sample after 1000 hr at 1700°C.

FIGURE 164 - Photomicrograph of molybdenum-50 wt % rhenium alloy after 60 days at 1200°C. (250X)

FIGURE 165 - Photomicrograph of molybdenum-50 wt % rhenium alloy after 180 days at 1200°C. (250X)

FIGURE 166 - Trace of the electron microprobe strip chart analysis of molybdenum-50 wt % rhenium alloy after 180 days at 1200°C.

FIGURE 167 - Photomicrograph of molybdenum-50 wt % rhenium alloy after 180 days at 1200°C, taken with backscattered electrons. (440X)

FIGURE 168 - Photomicrograph of molybdenum-50 wt % rhenium alloy after 180 days at 1200°C, taken with molybdenum $L\alpha$ radiation. (440X)

FIGURE 169 - Photomicrograph of molybdenum-50 wt % rhenium alloy after 180 days at 1200°C, taken with rhenium $L\alpha$ radiation. (440X)

FIGURE 170 - Photomicrograph of molybdenum-50 wt % rhenium alloy after 180 days at 1200°C, taken with cobalt $K\alpha$ radiation. (440X)

FIGURE 171 - Photomicrograph of molybdenum-50 wt % rhenium alloy after 180 days at 1200°C, taken with nickel $K\alpha$ radiation. (440X)

FIGURE 172 - Photomicrograph of molybdenum-50 wt % rhenium alloy after 180 days at 1200°C, taken with iron $K\alpha$ radiation. (440X)

FIGURE 173 - Photomicrograph of molybdenum-50 wt % rhenium alloy after 180 days at 1200°C, taken with chromium K α radiation. (440X)

FIGURE 174 - Microhardness traverse across molybdenum-50 wt % rhenium alloy after 180 days at 1200°C.

FIGURE 175 - Trace of the electron microprobe strip chart analysis of rhenium after 1000 hr at 1500°C.

FIGURE 176 - Photomicrograph of tungsten after exposure to $^{238}\text{PuO}_2$ microspheres for 532 days at 1000°C . (145X)

FIGURE 177 - Cross section of tungsten disc after 60 days at 1200°C . Original thickness = 1.63 mm. (58X)

FIGURE 178 - Cross section of tungsten disc after 365 days at 1200°C. Original thickness = 1.63 mm. (53X)

FIGURE 179 - Photomicrograph of tungsten after 60 days at 1200°C. (560X)

FIGURE 180 - Trace of the electron microprobe strip chart analysis of tungsten after 60 days at 1200°C.

FIGURE 181 - Trace of the electron microprobe strip chart analysis of tungsten after 90 days at 1200°C - Area "A".

FIGURE 182 - Trace of the electron microprobe strip chart analysis of tungsten after 90 days at 1200°C - Area "B" of photomicrograph in Figure 181.

FIGURE 183 - Photomicrograph of tungsten discs prior to testing
at 1200°C. (250X) (Etched)

FIGURE 184 - Comparison of the surface recession of tungsten compatibility discs with the low-pressure oxidation of tungsten at 1200°C.

FIGURE 185 - Trace of the electron microprobe strip chart analysis of tungsten after 2000 hr at 1500°C.

FIGURE 186 - Photomicrograph of a tungsten disc after 1000 hr at 1500°C. (250X)

FIGURE 187 - Trace of the electron microprobe strip chart analysis of tungsten after 1000 hr at 1500°C .

FIGURE 188 - Photomicrograph of a tungsten disc after 1000 hr at 1500°C, taken with tantalum $L\alpha$ radiation. (440X)

FIGURE 189 - Photomicrograph of tungsten disc after 1000 hr at 1500°C, taken with plutonium $M\alpha$ radiation. (440X)

FIGURE 190 - Photomicrograph of tungsten-26 wt % rhenium alloy after exposure to $^{238}\text{PuO}_2$ microspheres for 501 days at 1000°C . (145X)

FIGURE 191 - Photomicrograph of tungsten-26 wt % rhenium alloy after 60 days at 1200°C . (296X)

FIGURE 192 - Photomicrograph of tungsten-26 wt % rhenium alloy after 60 days at 1200°C, taken with backscattered electrons. (1760X)

FIGURE 193 - Photomicrograph of tungsten-26 wt % rhenium alloy after 60 days at 1200°C, taken with cobalt K α radiation. (1760X)

FIGURE 194 - Photomicrograph of tungsten-26 wt % rhenium alloy after 60 days at 1200°C, taken with iron $K\alpha$ radiation. (1760X)

FIGURE 195 - Photomicrograph of tungsten-26 wt % rhenium alloy after 60 days at 1200°C, taken with tungsten $L\alpha$ radiation. (1760X)

FIGURE 196 - Photomicrograph of tungsten-26 wt % rhenium alloy after 60 days at 1200°C, taken with rhenium $L\alpha$ radiation. (1760X)

FIGURE 197 - Photomicrograph of tungsten-26 wt % rehnium alloy after 60 days at 1200°C, taken with plutonium $M\alpha$ radiation. (1760X)

FIGURE 198 - Photomicrograph of tungsten-26 wt % rhenium alloy after 90 days at 1200°C. (560X)

FIGURE 199 - Trace of the electron microprobe strip chart analysis of tungsten-26 wt % rhenium alloy after 90 days at 1200°C.

FIGURE 200 - Photomicrograph of tungsten-26 wt % rhenium alloy after 365 days at 1200°C. (105X)

FIGURE 201 - Thickness of tungsten layer and width of intergranular reaction zone in tungsten-26 wt % rhenium alloy as a function of time.

FIGURE 202 - Photomicrograph of tungsten-26 wt % rhenium alloy after 1000 hr at 1500°C. (200X)

FIGURE 203 - Photomicrograph of corner of tungsten-26 wt % rhenium alloy disc after 1000 hr at 1500°C. (135X)

FIGURE 204 - Photomicrograph of hafnium after 1000 hr at 1500°C.
(23X)

FIGURE 205 - Trace of the electron microprobe strip chart analysis of hafnium after 1000 hr at 1500°C .

FIGURE 206 - Cross section of zirconium control specimen showing original configuration of specimen. (17X)

FIGURE 207 - Photomontage of zirconium specimen after 168 hr at 1700°C. (23.5X)

Table 1

FREE ENERGY OF REACTION FOR THE EQUATION $\text{Me} + \text{PuO}_2 \rightarrow \text{MeO}_x + \text{Pu}_2\text{O}_3$

Equation	Reference	ΔF in Kcal at Indicated Temperatures ($^{\circ}\text{K}$)						
		1200	1400	1600	1800	2000	2200	2400
$10\text{PuO}_2 + 2\text{Ta} \rightarrow \text{Ta}_2\text{O}_5 + 5\text{PuO}_2$	5	-1.7	-2.7	-4.9	-6.9	-10.1	-14.6	-20.2
$10\text{PuO}_2 + 2\text{Ta} \rightarrow \text{Ta}_2\text{O}_5 + 5\text{PuO}_2$	4	+36.3	+34.3	+31.1	+26.6	+14.4	-0.1	-17.2
$10\text{PuO}_2 + 2\text{Nb} \rightarrow \text{Nb}_2\text{O}_5 + 5\text{Pu}_2\text{O}_3$	5	+27.8	+24.9	+20.3	+14.3	+4.9	-5.2	-15.3
$4\text{PuO}_2 + \text{Nb} \rightarrow \text{NbO}_2 + 2\text{Pu}_2\text{O}_3$	5	+3.2	+2.2	+0.6	-0.9	-2.8	-5.1	-7.6
$2\text{PuO}_2 + \text{Nb} \rightarrow \text{NbO} + \text{Pu}_2\text{O}_3$	5	-1.6	-2.5	-3.7	-4.9	-6.4	-8.2	-10.0
$2\text{PuO}_2 + \text{Nb} \rightarrow \text{NbO} + \text{Pu}_2\text{O}_3$	4	+6.0	+4.9	+3.5	+1.8	-1.5	-5.3	-9.3
$6\text{PuO}_2 + \text{W} \rightarrow \text{WO}_3 + 3\text{Pu}_2\text{O}_3$	5	+85.8	+83.8	+81.0	+77.7	+71.6	+63.4	+53.3
$4\text{PuO}_2 + \text{W} \rightarrow \text{WO}_2 + 2\text{Pu}_2\text{O}_3$	5	+54.7	+53.0	+50.3	+46.5	+42.1		
$4\text{PuO}_2 + \text{W} \rightarrow \text{WO}_2 + 2\text{Pu}_2\text{O}_3$	4	+69.9	+67.8	+64.7	+59.9	+51.9		
$6\text{PuO}_2 + \text{Mo} \rightarrow \text{MoO}_3 + 3\text{Pu}_2\text{O}_3$	5	+105.6	+101.3	+94.8	+85.8	+76.1	+66.3	+56.5
$4\text{PuO}_2 + \text{Mo} \rightarrow \text{MoO}_2 + 2\text{Pu}_2\text{O}_3$	5	+61.9	+61.2	+59.9	+58.8	+57.3	+54.0	+47.1
$4\text{PuO}_2 + \text{Mo} \rightarrow \text{MoO}_2 + 2\text{Pu}_2\text{O}_3$	4		+76.0	+74.3	+72.2	+67.1	+58.8	+48.3
$4\text{PuO}_2 + \text{Re} \rightarrow \text{ReO}_2 + 2\text{Pu}_2\text{O}_3$	5	+90.1	+89.1	+86.6	+83.3	+79.4	+75.2	+70.8
$4\text{PuO}_2 + \text{Re} \rightarrow \text{ReO}_2 + 2\text{Pu}_2\text{O}_3$	4	+105.3	+103.9	+101.0	+96.7	+89.2	+80.0	+72.0
$8\text{PuO}_2 + \text{Re} \rightarrow \text{ReO}_4 + 4\text{Pu}_2\text{O}_3$	5	+196.4	+187.2	+177.2	+167.3	+156.6	+145.2	+133.7
$4\text{PuO}_2 + \text{Zr} \rightarrow \text{ZrO}_2 + 2\text{Pu}_2\text{O}_3$	5	-63.1	-62.8	-63.1	-63.3	-63.9	-64.2	-64.5
$4\text{PuO}_2 + \text{Zr} \rightarrow \text{ZrO}_2 + 2\text{Pu}_2\text{O}_3$	4	-47.9	-48.0	-48.7	-49.9	-54.1	-59.4	-63.3
$4\text{PuO}_2 + \text{Hf} \rightarrow \text{HfO}_2 + 2\text{Pu}_2\text{O}_3$	5	-66.9	-66.9	-67.5	-68.0	-69.0	-70.3	-71.8
$4\text{PuO}_2 + \text{Hf} \rightarrow \text{HfO}_2 + 2\text{Pu}_2\text{O}_3$	4	-51.7	-52.1	-53.1	-54.6	-59.2	-65.5	-70.6
$4\text{PuO}_2 + \text{Ti} \rightarrow \text{TiO}_2 + 2\text{Pu}_2\text{O}_3$	5	-29.8	-29.9	-30.5	-30.9	-31.8	-32.5	-34.7

Table 2

PARTIAL PRESSURES OF VAPOR COMPONENTS AS
A FUNCTION OF THE SUBSTOICHIOMETRY OF
PLUTONIUM-239 OXIDE^a

Temperature (°K)	Pressure (atm) ^a					Total Pressure
	<u>O</u>	<u>O₂</u>	<u>Pu</u>	<u>PuO</u>	<u>PuO₂</u>	
<u>Composition - PuO_{2.0}</u>						
1000	0.26E-25	0.39E-31	0.13E-26	0.93E-21	0.11E-21	0.10E-20
1200	0.75E-18	0.11E-20	0.49E-25	0.59E-18	0.10E-16	0.12E-16
1400	0.16E-12	0.32E-13	0.65E-24	0.60E-16	0.37E-13	0.23E-12
1600	0.16E-08	0.13E-07	0.45E-23	0.19E-14	0.17E-10	0.14E-07
1800	0.20E-05	0.29E-03	0.20E-22	0.28E-13	0.20E-08	0.29E-03
2000	0.62E-03	0.89E+00	0.67E-22	0.24E-12	0.90E-07	0.89E+00
2200	0.67E-01	0.63E+03	0.18E-21	0.14E-11	0.20E-05	0.63E+03
2400	0.33E+01	0.15E+06	0.41E-21	0.61E-11	0.27E-04	0.15E+06
2600	0.90E+02	0.15E+08	0.81E-21	0.21E-10	0.25E-03	0.15E+08
<u>Composition - PuO_{1.9}</u>						
1000	0.50E-26	0.14E-32	0.35E-25	0.46E-20	0.11E-21	0.47E-20
1200	0.86E-20	0.14E-24	0.33E-21	0.45E-16	0.90E-17	0.54E-16
1400	0.24E-15	0.74E-19	0.23E-18	0.32E-13	0.30E-13	0.62E-13
1600	0.53E-12	0.14E-14	0.31E-16	0.44E-11	0.13E-10	0.18E-10
1800	0.21E-09	0.31E-11	0.14E-14	0.20E-09	0.15E-08	0.19E-08
2000	0.25E-07	0.15E-08	0.30E-13	0.44E-08	0.65E-07	0.96E-07
2200	0.13E-05	0.22E-06	0.36E-12	0.54E-07	0.14E-05	0.30E-05
2400	0.33E-04	0.15E-04	0.29E-11	0.43E-06	0.19E-04	0.67E-04
2600	0.52E-03	0.51E-03	0.17E-10	0.25E-05	0.17E-03	0.12E-02
<u>Composition - PuO_{1.8}</u>						
1000	0.29E-26	0.48E-33	0.95E-25	0.74E-20	0.99E-22	0.75E-20
1200	0.16E-20	0.50E-26	0.74E-20	0.19E-15	0.70E-17	0.20E-15
1400	0.20E-16	0.51E-21	0.23E-16	0.27E-12	0.21E-13	0.29E-12
1600	0.24E-13	0.29E-17	0.97E-14	0.62E-10	0.82E-11	0.70E-10
1800	0.58E-11	0.24E-14	0.11E-11	0.43E-08	0.86E-09	0.51E-08
2000	0.48E-09	0.52E-12	0.45E-10	0.13E-06	0.36E-07	0.16E-06
2200	0.18E-07	0.43E-10	0.98E-09	0.20E-05	0.76E-06	0.28E-05
2400	0.35E-06	0.17E-08	0.13E-07	0.20E-04	0.96E-05	0.30E-04
2600	0.45E-05	0.38E-07	0.11E-06	0.14E-03	0.82E-04	0.23E-03

^a0.26E-25 is 0.26×10^{-25} atm

Table 2 (continued)

Temperature (°K)	Pressure (atm) ^a					Total Pressure
	<u>O</u>	<u>O₂</u>	<u>Pu</u>	<u>PuO</u>	<u>PuO₂</u>	
<u>Composition - PuO_{1.7}</u>						
1000	0.15E-26	0.12E-33	0.31E-24	0.12E-19	0.84E-22	0.12E-19
1200	0.41E-21	0.32E-27	0.83E-19	0.54E-15	0.51E-17	0.54E-15
1400	0.31E-17	0.12E-22	0.62E-15	0.11E-11	0.13E-13	0.11E-11
1600	0.25E-14	0.33E-19	0.50E-12	0.34E-09	0.48E-11	0.35E-09
1800	0.47E-12	0.15E-16	0.91E-10	0.29E-07	0.47E-09	0.30E-07
2000	0.30E-10	0.21E-14	0.58E-08	0.10E-05	0.19E-07	0.11E-05
2200	0.92E-09	0.12E-12	0.18E-06	0.19E-04	0.38E-06	0.19E-04
2400	0.16E-07	0.34E-11	0.30E-05	0.21E-03	0.46E-05	0.22E-03
2600	0.18E-06	0.58E-10	0.33E-04	0.17E-02	0.38E-04	0.17E-02
<u>Composition - PuO_{1.81}</u>						
1000	0.28E-27	0.43E-35	0.50E-23	0.37E-19	0.46E-22	0.37E-19
1200	0.10E-21	0.21E-28	0.79E-18	0.13E-14	0.31E-17	0.13E-14
1400	0.99E-18	0.12E-23	0.41E-14	0.23E-11	0.89E-14	0.24E-11
1600	0.96E-15	0.47E-20	0.25E-11	0.65E-09	0.34E-11	0.65E-09
1800	0.20E-12	0.28E-17	0.37E-09	0.51E-07	0.36E-09	0.52E-07
2000	0.14E-10	0.48E-15	0.20E-07	0.17E-05	0.14E-07	0.17E-05
2200	0.48E-09	0.32E-13	0.52E-06	0.29E-04	0.30E-06	0.30E-04
2400	0.88E-08	0.11E-11	0.80E-05	0.32E-03	0.38E-05	0.33E-03
2600	0.10E-06	0.20E-10	0.80E-04	0.24E-02	0.32E-04	0.25E-02

^a0.26E-25 is 0.26×10^{-25} atm

Table 3

MELTING POINTS AND VAPOR PRESSURES OF VARIOUS OXIDES^a

Oxide	Vapor Composition	Melting Point (°C)	Vapor Pressure at Indicated Temperatures (°K)						
			10^{-6} torr	10^{-5} torr	10^{-4} torr	10^{-3} torr	10^{-2} torr	10^{-1} torr	10^0 torr
TiO ₂	TiO ₂ , TiO, O ₂	1640	1800	1919	2053	2203	2377	2582	2825
ZrO ₂	ZrO ₂	2700	2060	2203	2350	2512	2679	2858	
HfO ₂	HfO ₂	2810	2270	2415	2570	2748	2951	3184	3443
MoO ₂	MoO ₃ , MoO ₂ , (MoO ₃) ₂		1368	1455	1550	1654	1762	1879	2004
MoO ₃	(MoO ₃) ₃ , (MoO ₃) ₄ , (MoO ₃) ₅	795	762	799	838	878	919	964	1038
WO ₂	WO ₂ , WO ₃		1641	1738	1848	1954	2075	2193	
WO ₃	(WO ₃) ₃ , (WO ₃) ₄ , (WO ₃) ₅	1473	1138	1262	1352	1409	1449	1489	
UO ₂	UO ₂	2176	1754	1884	2020	2133	2333	2535	2786
MnO	Elements	1650	1384	1502	1622	1758	1901	2056	2223
FeO	Elements	1420	1413	1521	1644	1774	1914	2070	2239
NiO	Elements	1800	1300	1400	1510	1629	1758	1898	2046
CoO	Elements	2090	1368	1476	1570	1683	1824	1972	2138
ZnO	Elements	1969	1002	1069	1144	1230	1330	1445	1592

Table 4

SUMMARY OF THE OXYGEN SOLUBILITY LIMITS IN REFRACTORY METALS, AND THE PHASE RELATIONSHIPS
THAT EXIST BETWEEN THESE METALS AND METALLIC IMPURITIES FOUND IN THE PLUTONIUM DIOXIDE

Impurity	Tantalum	Niobium	Molybdenum	Tungsten	Rhenium
	O solubility limit in Ta:	O solubility limit in Nb:	O solubility limit in Mo:	O solubility limit in W:	O solubility limit in Re:
O	1800°C ~ <5.0 at. %	1915°C ~ 9 at. %	1649°C - 0.018 at. %	1700°C - 0.06 at. %	no data available
x	1650°C - 6.4 at. %	1700°C ~ 7 at. %			
y	1500°C ~ 3.7, 4.6 at. %	1500°C ~ 5 at. %			
g	1300°C - 4.2 at. %	1200°C ~ 3 at. %			
e	1100°C - 3.1 at. %	1000°C ~ 2 at. %			
n	1000°C - 3.0 at. %				
C	Cr solubility limit in Ta	Cr solubility limit in Nb	Complete solid	Complete solid	Cr solubility in Re
h	1900°C ~ 18 at. %	1900°C ~ 19 at. %	solubility	solubility above 1495°C	1900°C ~ 12 at. %
r	1700°C ~ 13 at. %	1717°C ~ 27 at. % (max)		1200°C ~ 17 at. %	1700°C ~ 10 at. %
o	1500°C ~ 10 at. %	1500°C ~ 19.6 at. %		1000°C ~ 10 at. %	1500°C ~ 9 at. %
m	1200°C ~ 9 at. %	1200°C ~ 11 at. %			1200°C ~ 7 at. %
i	-----	1000°C ~ 8 at. %			1000°C ~ 5 at. %
u	TaCr ₂ mp. at 2020°C	-----			-----
m		CbCr ₂ mp. at 1740°C			Cr ₂ Re ₃ melts at 2350°C
	Fe solubility limit in Ta	Fe solubility limit in Nb	Fe solubility limit in Mo	Fe solubility limit in W	Fe solubility limit in Re
	(no available data)	1900°C ~ 3 at. %	1700°C ~ 19 at. %	1640°C - 2.6 at. %	(no available data)
	-----	1700°C ~ 4 at. %	1540°C ~ 22 at. % (max)	-----	-----
I	TaFe ₃ mp. 1775°C	1500°C ~ 4 at. %	1200°C ~ 6 at. %	W ₂ Fe ₃ mp. 1640°C	Re ₂ Fe ₃ mp. >1500°C
r	TaFe(?)	1200°C ~ 3 at. %	1000°C ~ 3 at. %		
o	Eutectic melting ~1350°C	1000°C ~ 2 at. %	-----		
n	Ta-TaFe(?)	-----	o (50 at. % Fe) mp. 1540°C		
		Cb ₃ Fe ₂ mp. ~1800°C	Mo ₂ Fe ₃ mp. ~1480°C		
		Cb ₁₈ Fe ₂₁ 600 to 1500°C			
		CbFe ₂ mp. 1655°C			
C	Co solubility in Ta	Co solubility in Nb	Co solubility in Mo	Co solubility in W	Complete solid solubility
o	(no available data)	(no available data)	1620°C - 11.5 at. % (max)	1600°C ~ 0.9 at. %	
b	probably less than 5 at. %	probably less than 5 at. %	1480°C - 4.4 at. %		
	-----	-----	1200°C - 1.5 at. %		
a	TaCo ₂ mp. 1593°C	NbCo mp. ~ 1475°C	1100°C - 0.95 at. %		
l		NbCo ₂ mp. ~ 1540°C	-----		
t			o (40 at. % Cu) ~1250 to	W ₆ Co ₇ mp. ~ 1630°C	
			~1585°C mp.		
			Mo ₆ Co ₇ mp. ~ 1500°C		
	Ni solubility in Ta	Ni solubility in Nb	Ni solubility in Mo	Ni solubility in W	Ni solubility in Re
N	1600°C ~ 6 at. %	1700°C ~ 2 at. %	1700°C ~ 2 at. %	~1500°C ~ 0.9 at. % (max)	1700°C ~ 50 at. %
i	1300°C ~ 0.5 at. %	1500°C ~ 3 at. %	1500°C ~ 2 at. %	-----	1600°C ~ 55 at. %
	-----	1320°C ~ 4.5 at. % (max)	1360°C ~ 1.8 at. %	No compounds stable	1500°C ~ 52 at. %
k	TaNi mp. ~ 1570°C	1200°C ~ 4 at. %	1200°C ~ 1 at. %	above 1000°C	1200°C ~ 51 at. %
e	TaNi ₂ mp. ~ 1420°C	1000°C ~ 3 at. %	1000°C ~ <1 at. %		1000°C ~ 50 at. %
l	TaNi ₃ mp. ~ 1530°C	-----	-----		-----
		CbNi mp. ~ 1320°C	MoNi mp. ~ 1360°C		No compounds in system
		CbNi ₃ mp. ~ 1430°C			
M	No solid solubility	No solid solubility	No solid solubility	No data available	No data available on
a	data available	data available	data available		Re-rich compositions:
n	-----	-----	-----		-----
g	TaMn ₂ mp. ~1500°C	NbMn ₂ mp. ~ 1500°C	Possible intermetallic		o phase MnRe
a			compounds at 64 at. % Mn		
e			and 80-88 at. % Mn		
s					
e					

Table 5

SUMMARY OF IMPURITY DIFFUSION IN REFRACTORY METALS

<u>Impurity</u>	<u>Tantalum</u>	<u>Niobium</u>
O ^a	See Figure 4	See Figure 4
Fe ^a	$D=0.505 \exp \frac{(-71,400)}{RT} \text{ cm}^2/\text{sec}$ (Low Fe concentrations)	
Cr ^b		

<u>Impurity</u>	<u>Molybdenum</u>	<u>Tungsten</u>												
O ^a														
Fe ^a	$D=2.8 \times 10^{-6} \exp \frac{(-34,800)}{RT} \text{ cm}^2/\text{sec}$	$D=1.4 \times 10^{-2} \exp \frac{(-66,000)}{RT} \text{ cm}^2/\text{sec}$												
	<table><tr><th><u>Temp °C</u></th><th><u>D, cm²/sec</u></th></tr><tr><td>900</td><td>7.1×10^{-15}</td></tr><tr><td>1100</td><td>1.5×10^{-11}</td></tr><tr><td>1275</td><td>2.3×10^{-11}</td></tr><tr><td>1500</td><td>4.2×10^{-10}</td></tr><tr><td>1700</td><td>1.9×10^{-10}</td></tr></table> (Low Fe concentrations)	<u>Temp °C</u>	<u>D, cm²/sec</u>	900	7.1×10^{-15}	1100	1.5×10^{-11}	1275	2.3×10^{-11}	1500	4.2×10^{-10}	1700	1.9×10^{-10}	
<u>Temp °C</u>	<u>D, cm²/sec</u>													
900	7.1×10^{-15}													
1100	1.5×10^{-11}													
1275	2.3×10^{-11}													
1500	4.2×10^{-10}													
1700	1.9×10^{-10}													
Cr ^b	$D=4.3 \exp \frac{(-72,700)}{RT} \text{ cm}^2/\text{sec}$ (For 9.9 wt % Cr alloy)													

^a See Reference 15^b See Reference 16

Table 6

PENETRATION MEASUREMENTS ON TANTALUM AT 1200°C

<u>Time at 1200°C (days)</u>	<u>Minimum Thickness (μm)</u>
60	1570 (1500 at one area)
92	1600
92	1580
180	1610
180	1680

Table 7

SUMMARY OF VARIABLE PURITY TESTS^a

- a) High purity base composition (60-day exposure only)
0.01 wt % Fe, 0.003 wt % Cr.
- b) 0.06 wt % Fe, 0.05 wt % Cr
- c) 0.16 wt % Fe, 0.14 wt % Cr
- d) 0.27 wt % Fe, 0.26 wt % Cr
- e) 0.35 wt % Fe, 0.33 wt % Cr
- f) 0.06 wt % Fe, 0.40 wt % Cr
- g) 0.44 wt % Fe, 0.06 wt % Cr

^aComposition given as % of Pu²³⁸

Table 8

THE EFFECTS OF THE IRON AND CHROMIUM CONTENT IN $^{238}\text{PuO}_2$ ON THE COMPATIBILITY OF TANTALUM-10 wt % TUNGSTEN

Fuel Composition ^d	Time at 1200°C (days)	Fe-Rich ^a Surface Compound Thickness (μm)	Maximum ^a Fe Intensity	Maximum ^a Fe Penetration (μm)	Cr-Rich ^a Surface Compound Thickness (μm)	Maximum ^a Cr Intensity	Maximum ^a Cr Penetration (μm)	Approximate Depth of Intergranular Attack at Base (μm)	Comments
Base Composition 0.01% Fe, 0.003% Cr	60	zero	0.5×10^4	≈25	zero	0.5×10^4	≈10 ^b	100 to 400	Cr present in grain boundary 40 μm below surface
0.06% Fe, 0.05% Cr, remainder PuO ₂	30	2	$>5 \times 10^4$	2	2	2×10^4	2	100	
	60							140	
	120	6	4×10^5	15	4	4×10^5	10	90	
0.16% Fe, 0.14% Cr, remainder PuO ₂	30	4	$>1 \times 10^5$	8	4	2×10^4	6	130	
	60							110	
	120	6	3×10^5	12	4	3×10^5	6	170	
0.27% Fe, 0.26% Cr, remainder PuO ₂	30	5	$>10^5$	14	4	5×10^4	6	100	Cr present in grain boundary at 60, 120, & 150 μm below surface
	60							160	
	120	7	4×10^5	16	7	4×10^5	12	40	
0.35% Fe, 0.33% Cr, remainder PuO ₂	30	12	2×10^5	22	12	$>10^5$	18	150	Cr present at 18 to 25 μm below surface
	60							230	
	120	11	5×10^5	≈30	10	2×10^5	18	530	
0.06% Fe, 0.40% Cr, remainder PuO ₂	30	≈50	3×10^4	≈50	≈50	2×10^4	≈50	110	
	60							210	
	120	4	1×10^5	10	4	4×10^5	8	90	
0.44% Fe, 0.06% Cr, remainder PuO ₂	30°	≈25 ^b	2×10^5	≈35 ^b	≈25 ^b	5×10^4	≈30 ^b	100	
	60							30	
	120	zero	3×10^4	8	zero	1×10^4	4	90	

^aSee Figure 45 for explanation of column headings. Surface compound is believed to be Ta(Fe,Cr)₂ Laves phase based on the tantalum content of the phase.

^bProbe analysis conducted at a "high" traverse speed; depth of penetration measurements are less accurate than other specimens.

^cSidewall of capsule was analyzed; base fractured during metallurgical sectioning.

^dComposition given as % of ^{238}Pu .

Table 9

OXIDE PENETRATION INTO TANTALUM-10 wt % TUNGSTEN AT 1700°C

<u>Time at 1700°C (hr)</u>	<u>Depth of Oxide Penetration (μm)</u>
12	36
24	40
48	138 to 201
96	93 (measured in weld zone)
1000	820

Table 10

DEPTH OF PENETRATION DATA FOR T-222 AT 1000°C

<u>Time (hr)</u>	<u>Depth of Penetration ΔX (μm)</u>	<u>ΔX^2 (μm^2)</u>
3552	12.8	163
6768	22.7	515
12768	26.2	690

Table 11

DEPTH OF PENETRATION DATA FOR T-222 AT 1200°C

<u>Time (days)</u>	<u>Time (hr)</u>	<u>General Reaction Thickness ΔX_s (μm)</u>	<u>ΔX_s^2 (μm^2)</u>	<u>Intergranular Penetration ΔX_i (μm)</u>	<u>ΔX_i^2 (μm^2)</u>
40	960	5 - 15	25 - 225	50 - 70	2500-4900
60	1440	30 - 55	900 - 3030	115 - 135	13200-18200
90	2160	65 - 88	4230 - 7750	116 - 132	13500-17400
180	4320	26	676	150 - 165	22500-27200

Table 12

DEPTH OF PENETRATION DATA FOR T-111 AT 1700°C

<u>Time (hr)</u>	<u>Depth of Plutonia-Hafnia Intergranular Penetration (μm)</u>
24	40
48	80-100
200	192-216
500	178
1000	132-259

Table 13

SUMMARY OF THE DEPTH OF IMPURITY
PENETRATION IN MOLYBDENUM AT 1200°C

<u>Time (days)</u>	<u>Depth of Intergranular Penetration (μm)</u>
32	8
60	14
90	78-95
180	47-95
343	none observed

Table 14

SUMMARY OF THE DEPTH OF TITANIUM BEARING
PARTICLES IN TZM AFTER EXPOSURE AT 1200°C

<u>Time (days)</u>	<u>Depth (μm)</u>
32	26
62	30
90	20-32
180	35
360	26

Table 15

SUMMARY OF THE DEPTH OF TITANIUM BEARING
PARTICLES IN TZM AFTER EXPOSURE AT 1500°C

<u>Time (hr)</u>	<u>Depth (μm)</u>
48	-
96	24
200	24
500	40
1000	50

Table 16

SUMMARY OF THE DEPTH OF TITANIUM BEARING
PARTICLES IN TZM AFTER EXPOSURE AT 1700°C

<u>Time (hr)</u>	<u>Maximum Depth (μm)</u>
12	130
24	115
48	190
96	210
200	310
500	360
1000	390

Table 17

THICKNESS OF IMPURITY LAYER
IN Mo-50 wt % Re ALLOY AT 1200°C

<u>Time (days)</u>	<u>Reaction Depth (μm)</u>
32	26-28
60	31-36
90	23-25 32-34
180	26-32 35-41

Table 18

SUMMARY OF THE SURFACE RECESSION MEASUREMENTS FOR
 TUNGSTEN DISCS IN CONTACT WITH $^{238}\text{PuO}_2$ at 1200°C .
 THE DISCS AND FUEL WERE WELD-SEALED INSIDE
 TUNGSTEN-26 wt % RHENIUM CONTAINERS.

<u>Time at 1200°C (days)</u>	<u>Surface Recession (μm per side)</u>	
	<u>Minimum (peaks)</u>	<u>Maximum (crevices)</u>
60	40	140
60	50	150
90	30	100
90	60	110
180	80	210
180	60	110
365	130	380

APPENDIX A

Table A-1

SUMMARY OF 1000°C COMPATIBILITY TESTS

<u>Liner Material</u>	<u>Time (days)</u>	<u>Capsule Design</u>
Tantalum	132, 266, 516, (1377)	D-1
SGS Tantalum	132, 266, 516, (1377)	D-1
Ta-10 wt % W	132, 266, 516, (1377)	D-1
T-222	148, 282, 532, (1393)	D-1
Tungsten	133, 282, 532, (1393)	D-1
W-25 wt % Re	216, 501, (1326), (1364)	D-1

() = samples still in furnace - number means the total time in the furnace in days as of 11/15/69.

Table A-2

SUMMARY OF 1200°C COMPATIBILITY TESTS

<u>Liner Material</u>	<u>Time (hr)</u>					<u>Capsule Design</u>	<u>Fuel Sample Number</u>	<u>Material Analysis Number</u>
	<u>30</u>	<u>60</u>	<u>90</u>	<u>180</u>	<u>360</u>			
Tantalum	C	C	C	C	C(291 days)	D-2	PPX-25	632
Ta-10 wt % W	C	C	C	C	C	D-2	MS-45 P-377-378	570,571
T-222	C	C	C	C	2/28/70	D-2	MS-45	566
Molybdenum	C	C	M	M	C(343 days)	D-3	P-377-378 MS-59-3	634
TZM	C	C	C	C	M	D-4	P-377-378	635
Mo-50 wt % Re	C	C	C	C	C(343 days)	D-3	P-377-378 MS-59-3	710
Tungsten	C	C	C	C	C	D-5	P-377-378	458
W-26 wt % Re	C	C	C	C	C	D-5	P-377-378	633

F = In Furnace
M = In Metallography
C = Completed

Table A-3

SUMMARY OF 1500°C COMPATIBILITY TESTS

Liner Material	Time (hr)									Capsule Design	Fuel Sample Number	Material Analysis Number
	12	24	48	96	168	200	500	1000	2000			
Tantalum	C	C	C	C	C	P	P	C	P	D-6 D-7	{ MS-45 MS-46 PPX-25	Capsule - 472 Plug - 473
Ta-10 wt % W	-	-	C	C	-	C	C	C	C	D-6	{ MS-45 MS-46	Capsule - 487 Plug - 488
T-111	-	-	P	P	-	P	P	C	P	D-7	PPX-25	Capsule - A Plug - B
T-222	-	-	P	P	-	P	P	P	P	D-7		
Niobium	-	-	-	-	-	-	-	C	-	D-7	{ MS-45 MS-46	
	C	C	C	C	C	-	C ^a	-	P	D-6	PPX-25	Capsule - 460 Plug - 461
Molybdenum	-	-	C	C	-	C	C	C	C	D-6	{ MS-45 MS-46	Capsule - 474 Plug - 475
TZM	-	-	C	C	-	C	C	C	C	D-6	{ MS-45 MS-46	
Mo-50 wt % Re	-	-	P	P	-	P	P	P	P	D-9		
Rhenium	-	-	P	P	-	P	P	C	P	D-8	PPX-25	764
Tungsten	-	-	C	C	-	C	C	C	C	D-6	{ MS-45 MS-46	Capsule - 457 Plug - 458
	-	-	-	-	-	-	-	C	-	D-8	PPX-25	Plug - 458
W-26 wt % Re	-	-	P	P	-	P	P	C	P	D-8	PPX-25	797
Hafnium	P	P	P	P	P	-	-	C	P	D-8	PPX-25	550
Zirconium	-	-	-	M	-	F	-	-	-	D-7	MS-59-3SP D PPX-25	
	M ^b	M	P	-	P	-	-	-	-			

P = Proposed Tests; F = In Furnace; M = In Metallography; C = Completed

^a 375 hr^b 4 hr

Table A-4
SUMMARY OF 1700°C COMPATIBILITY TESTS

Liner Material	Time (hr)									Capsule Design	Fuel Sample Number	Material Analysis Number
	12	24	48	96	168	200	500	1000	2000			
Tantalum	C	C	C	C	-	C	C	P	-	D-6	MS-59-3SP MS-46	Capsule - 472 Plug - 473
Ta-10 wt % W	C	C	C	C	-	C	C	C	-	D-6	MS-59-3SP MS-46	Capsule - 487 Plug - 488
T-111	P	C	C	P	-	C	C	C	-	D-6	MS-59-3SP	Capsule - A Plug - B
T-222	-	P	P	P	-	P	P	P	-	D-7		
Niobium	C	C	C	C	C	C	C	P	-	D-6	MS-46	Capsule - 460 Plug - 461
Molybdenum	C	C	C	C	-	C	C	C	-	D-6	MS-59-3SP MS-46	Capsule - 474 Plug - 475
TZM	C	C	C	C	-	C	C	C	-	D-6	MS-59-3SP	C
Mo-50 wt % Re	-	P	P	P	-	P	P	P	-	D-9		
Rhenium	-	P	P	P	-	P	P	M	-	D-8	PPX-25	764
Tungsten	-	P	P	P	-	P	P	M	F	D-8	PPX-25	Capsule - 457 Disc & Plug - 458
W-26 wt % Re	-	P	P	P	-	P	P	M	F	D-8	PPX-25	797
Hafnium	P	P	P	P	P	-	-	M	-	D-8	PPX-25	550
Zirconium	-	C	C	C	C	-	-	-	-	D-6	MS-59-3SP	D

P = Proposed Tests
F = In Furnace
M = In Metallography
C = Completed

Table A-5
SUMMARY OF 1900°C COMPATIBILITY TESTS

<u>Liner Material</u>	<u>Time (hr)</u>						<u>Capsule Design</u>	<u>Fuel Sample Number</u>	<u>Material Analysis Number</u>
	<u>24</u>	<u>48</u>	<u>96</u>	<u>200</u>	<u>500</u>	<u>1000</u>			
Tantalum	M	-	-	-	M	-	D-6	PPX-25	Capsule - 472
	-	M	M	M	-	P	D-7	MS-59-3SP	Plug - 473
Ta-10 wt % W	M	-	-	-	M	-	D-6	PPX-25	Capsule - 487
	-	M	M	M	-	P	D-7	MS-59-3SP	Plug - 488
T-111	M	-	-	-	M	-	D-6	PPX-25	Capsule - A
	-	M	M	M	-	P	D-7	MS-59-3SP	Plug - B
T-222	P	P	P	P	P	P	D-7		
Niobium	M	-	-	-	M	-	D-6	PPX-25	Capsule - 460
	-	M	M	M	-	P	D-7	MS-46	Plug - 461
Molybdenum	C	-	-	-	C	-	D-6	PPX-25	Capsule - 474
	-	C	C	C	-	P	D-7	MS-59-3SP	Plug - 475
TZM	M	-	-	-	M	-	D-6	PPX-25	C
	-	M	M	M	-	P	D-7	MS-59-3SP	
Mo-50 wt % Re	P	P	P	P	P	P	D-9		
Rhenium	P	M	M	M	P	P	D-8	PPX-25	764
Tungsten	P	M	M	M	P	P	D-8	PPX-25	Capsule - 457
									Plug - 458
W-26 wt % Re	P	M	M	M	P	P	D-8	PPX-25	797
Hafnium	P	M	M	M	P	P	D-8	PPX-25	550

P = Proposed Tests
F = In Furnace
M = In Metallography
C = Completed

Table A-6

PROPOSED TESTS AT 2100°C

<u>Materials</u>	<u>Time Periods (hr)</u>
Ta, Nb, Hf	4, 8, 12, 24, 48
Ta-10 wt % W, T-111, T-222, Mo, TZM, Mo-50 wt % Re, W, W-25 wt % Re, Re	8, 16, 32, 64, 128

APPENDIX B

APPENDIX B
SUMMARY OF CHEMICAL ANALYSES OF CAPSULE MATERIALS

Sample Analysis Number	Material	Elements													
		Ag	Al	Au	B	C	Ca	Cd	Co	Cr	Cu	Fe	H	Hf	Mg
632	Ta		<0.0005			0.004				N.D. <0.001	0.0008	0.001	0.0002		<0.0005
472	Ta	N.D. <0.0005				0.008				N.D. <0.001	0.001	0.001	0.0004		N.D. <0.0005
473	Ta	N.D. <0.0005				0.003				N.D. <0.001	0.001	0.009	0.0001		N.D. <0.0005
570	Ta-10 wt % W		0.001			0.005				N.D. <0.001	0.001	0.03	0.0001		
571	Ta-10 wt % W		0.0005			0.004				N.D. <0.001	0.001		0.0002		<0.0005
487	Ta-10 wt % W		<0.0005			0.002				N.D. <0.001	N.D. <0.001	0.002	0.0004		<0.0005
488	Ta-10 wt % W		0.0005			0.004				N.D. <0.001	N.D. <0.001	0.002	0.0001		<0.0005
A	T-111		0.002			0.002				0.01	0.005	0.005	0.001	2.2	
B	T-111		0.08			0.004				0.01		0.006	0.001	2.2	
566	T-222		0.0008 0.0008			0.006				N.D. <0.001	<0.001	0.005	0.0002	0.25	<0.0005
460	Nb		N.D. <0.0005		N.D. <0.001	0.005	N.D. <0.05	N.D. <0.01	N.D. <0.005	N.D. <0.001	N.D. <0.005	0.002	0.0001	N.D. <0.005	<0.0005
461	Nb		N.D. <0.0005		N.D. <0.001	0.004	N.D. <0.05	N.D. <0.01	N.D. <0.005	N.D. <0.001	N.D. <0.005	0.002	0.0001	N.D. <0.005	<0.0005
634	Mo					0.013	N.D. <0.1			N.D. <0.005	<0.0005	0.02	0.0001		<0.0005
474	Mo					0.003	N.D. <0.05			N.D. <0.005	0.003	0.008	0.0001		<0.0005
475	Mo					0.001	N.D. <0.05			N.D. <0.005	0.004	0.01	0.0001		<0.0005
635	TZM		N.D. <0.005			0.030				<0.005	N.D. <0.005	0.004	0.0001		<0.0005
C	TZM		0.01			0.016				N.D. <0.001	0.15	0.005	0.0001		<0.0005
710	Mo-50 wt % Re		0.001			0.016				0.003	N.D. <0.005	0.015	<0.0001		
764	Re		0.0005	N.D. <0.005		<0.005	N.D. <0.05					0.035	0.0004		<0.0005
457	W					0.0005	N.D. <0.01					0.006	0.0001		<0.0005
458	W					0.005	N.D. <0.01					0.01	0.0001		<0.0005
633	W-26 wt % Re		<0.0005			0.006				0.003	0.0005	0.1	0.0001		<0.0005
797	W-26 wt % Re		0.001	N.D. <0.005		0.002	N.D. <0.05			0.03		0.1	<0.0001		N.D. <0.001
D	Zr		0.0005			0.007					0.0007	0.01	0.0028		<0.0005
550	Hf		0.003			0.004					<0.0005	0.02	0.0007	major	<0.0005

APPENDIX B (continued)

Sample Analysis Number	Material	Elements																Total Impurities
		Mn	Mo	N	Na	Nb	Ni	O	Pb	Re	Si	Sn	Ta	Ti	V	W	Zr	
632	Ta	<0.0005	N.D. <0.005	0.0012		0.03	N.D. <0.005	0.0033	0.001		<0.0005	N.D. <0.001	major	N.D. <0.001				<0.056
472	Ta	N.D. <0.0005	N.D. <0.005	0.0006	N.D. <0.05	0.006	N.D. <0.005	0.0014			N.D. <0.001	N.D. <0.001	major	N.D. <0.001				<0.084
473	Ta	N.D. <0.0005	N.D. <0.005	0.0032	N.D. <0.05	0.006	N.D. <0.005	0.0017			N.D. <0.001	N.D. <0.001	major	N.D. <0.001				<0.090
570	Ta-10 wt % W		0.003	0.0124		0.03	<0.005	0.0182		0.003			major	N.D. <0.001		10.5		<0.111
571	Ta-10 wt % W		0.002	0.0016	0.01		N.D. <0.005	0.0098			<0.0005		major	N.D. <0.001		9.8		<0.037
487	Ta-10 wt % W	0.0005	N.D. <0.005	0.0008		0.007	N.D. <0.005	0.0008			N.D. <0.001		major	N.D. <0.001		major		<0.028
488	Ta-10 wt % W	0.0005	N.D. <0.005	0.0031		0.04	N.D. <0.005	0.0026			N.D. <0.001		major	N.D. <0.001		major		<0.063
A	T-111	0.001	0.01	0.003		0.01		0.002			0.005		major			8.6	0.03	<0.086
B	T-111	0.001	0.005	0.003		0.01		0.002			0.001		major	0.003		8.6	0.03	<0.156
566	T-222		N.D. <0.005	0.0035		0.005	<0.005	0.0036			<0.0005		major	N.D. <0.001		8.4	0.01	<0.048
460	Nb	<0.0005	N.D. <0.005	0.0037		major	N.D. <0.005	0.0104	N.D. <0.001		0.0005	N.D. <0.001	N.D. <0.01	N.D. <0.001	N.D. <0.005	N.D. <0.01	N.D. <0.001	<0.139
461	Nb	<0.0005	N.D. <0.005	0.0034		major	N.D. <0.005	0.0133	N.D. <0.001		N.D. <0.0005	N.D. <0.001	N.D. <0.01	N.D. <0.001	N.D. <0.005	N.D. <0.01	N.D. <0.001	<0.137
634	Mo	N.D. <0.0005	major	0.0004			N.D. <0.005	0.0125		0.02			N.D. <0.01	N.D. <0.001		N.D. <0.05		<0.238
474	Mo	N.D. <0.0005	major	0.0002			N.D. <0.005	0.0018		0.003			N.D. <0.01	N.D. <0.001		N.D. <0.01		<0.101
475	Mo	N.D. <0.0005	major	0.0002			N.D. <0.005	0.0024		0.003			N.D. <0.01	N.D. <0.001		N.D. <0.01		<0.103
635	TZM		major	0.0005		N.D. <0.005	N.D. <0.005	0.0017		0.001				≥0.3		N.D. <0.05	0.02	<0.113
C	TZM		major	0.0005		N.D. <0.005	N.D. <0.005	0.0016	0.003		N.D. <0.001			0.75		N.D. <0.01	0.02	<0.209
710	Mo-50 wt % Re		major	0.0003		N.D. <0.005	0.003	0.0009		51.0	0.001			N.D. <0.001		N.D. <0.01		<0.061
764	Re	0.0005		0.0001	0.0015			0.0036		major	N.D. <0.001							<0.103
457	W	N.D. <0.0005	0.009	0.0001		N.D. <0.0005	N.D. <0.001	0.0009			N.D. <0.0005			0.0009		major		<0.030
458	W	N.D. <0.0005	0.005	0.0001		N.D. <0.005	N.D. <0.001	0.0008			N.D. <0.005			0.005		major		<0.048
633	W-26 wt % Re		N.D. <0.005	0.0004		N.D. <0.005	N.D. <0.005	0.0106	0.001	25.5	0.0008			<0.001		major		<0.139
797	W-26 wt % Re	N.D. <0.001	0.001		0.0002	N.D. <0.005	0.005	0.0081		25.0	0.004			N.D. <0.001		major		<0.214
D	Zr			0.0002				0.0018			0.006			N.D. <0.001			major	<0.030
550	Hf			0.0099				0.021						0.002		N.D. <0.01	0.6	<0.672

APPENDIX C

APPENDIX C

CHEMICAL ANALYSES OF FUEL SAMPLES
USED IN REFRACTORY METALS COMPATIBILITY TESTS

Batch Number	Composition (wt %)								
	Al	B	Ca	Co	Cr	Cu	Fe	Mg	Mn
MS-45	0.09	0.03	0.07	0.42	0.32	0.01	0.46	0.12	0.11
MS-46	0.08	0.06	0.03	0.11	0.11	-	0.66	0.01	-
P-377-378	-	-	0.03	0.11	0.09	-	0.28	0.01	-
PPX-25	0.09	<0.03	0.08	-	0.08	<0.03	0.47	0.04	<0.01
MS-59-3SP	0.11	0.04	0.07	0.28	0.41	<0.04	0.36	0.07	0.06

Batch Number	Composition (wt %)							
	Mo	Na	Ni	Pb	Si	Sn	Zn	Total
MS-45	-	-	0.07	0.44	-	-	0.11	2.25
MS-46	-	-	0.06	-	-	-	0.07	1.19
P-377-378	-	-	-	-	-	-	-	0.52
PPX-25	-	trace	<0.04	-	trace	-	0.08	0.95
MS-59-3SP	<0.14	trace	0.05	0.23	trace	trace	0.04	1.90

APPENDIX D

FIGURE D-1

FIGURE D-2

FIGURE D-3

FIGURE D-4

FIGURE D-5

Material being tested

Tantalum
Ta-10 wt % W
T-111 alloy
Niobium
Molybdenum
TZM alloy
Zirconium
Tungsten

FIGURE D-6

Materials Being Tested

Tantalum
Tantalum-10 wt % Tungsten
T-111 alloy
Niobium
Molybdenum
TZM alloy
Zirconium
T-222

FIGURE D-7

Materials being Tested

Rhenium
Hafnium
Tungsten-26 wt % Rhenium
Tungsten
Iridium
Rhodium

FIGURE D-8

FIGURE D-9

APPENDIX E

APPENDIX E

SUMMARY OF ETCHANTS FOR VARIOUS REFRACTORY METALS AND ALLOYS

Material	Etchant	Remarks
Ta, Ta-10 wt % W, T-111, T-222, Nb	60 ml lactic acid 20 ml HNO ₃ 20 ml HF	Immerse 1/2-3 min at room temperature
Mo, TZM, Mo-50 wt % Re	20 ml H ₃ PO ₄ 20 ml HNO ₃ 0.2 g Cr ₂ O ₃	Immerse 1/2-3 min 30-45°C
Re, W-26 wt % Re	5 g KCN 25 ml H ₂ O	20 V ac
W	60 ml lactic acid 20 ml HNO ₃ 10 ml HF	Immerse or swab 10 sec at 20-30°C
Hf, Zr	45 ml HNO ₃ 10 ml HF 45 ml H ₂ O	Immerse 5-10 sec