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A Thermodynamic Study of the MWG System/Components and Measurement of the Oxygen Partial Pressure in the Heat Source Capsule

Donald J. David

June 23, 1980

Monsanto

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Miamisburg, Ohio 45342

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Summary

A thermodynamic study of the Milliwatt Generator heat source capsule was performed to determine the effects of the oxide fuel on container materials at elevated temperatures in order to evaluate the factors affecting embrittlement of T-111 alloy. The study indicates that relatively slow oxidation of the T-111 alloy of the capsule occurs during pretreatment. Yttrium added to the $^{238}\text{PuO}_2$ fuel charge is functioning in its designed role as an oxygen getter and is stabilizing at an O/Pu ratio of 1.75. The free energy of formation of hafnium oxide has been measured and found to be -70632 cal/mole; this suggests that the ability of hafnium to strongly function as an oxygen getter may be largely determined by the kinetics, and the free energy may play a lesser role.

Introduction

The alloy T-111, which consists of 90% tantalum, 8% tungsten, and 2% hafnium, is being used as the encapsulating liner and strength member for the isotopic fuel in thermoelectric generators. This material was selected because of its high strength, long service life, and ability to contain the isotopic fuel $^{238}\text{PuO}_2$ under a variety of environments.

Unfortunately, tantalum-base alloys such as T-111 readily pick up reactive gases like oxygen at elevated temperatures [1-4]. At these temperatures these gases may react interstitially or with the more reactive elements of the alloy. In the latter case a coherent precipitate results, and in either of the two cases the net result is one that strengthens the material [5-8]. However, this strengthening process results in loss of ductility and increase in hardness (embrittlement) even when exposed to only the parts-per-million range of oxygen and, therefore, an overall loss in the desirable physical and mechanical properties [9-12].

During the course of development of the radioisotopic heat sources, it has been established that yttrium added to the $^{238}\text{PuO}_2$ fuel as an oxygen getter improved the compatibility between the plutonia and the T-111 alloy container [13]. Further studies at 1300-1400°C for 1 hr showed that a heat treatment after loading was beneficial to the properties of T-111. This heat treatment accomplished two results: 1) a loss of coherency of the HfO_2 precipitate, which grows into discrete rectangular particles that migrate toward the grain boundaries, and therefore restores the ductility of the alloy up to gas exposures of about 3500 ppm O_2 [8,14]; and 2) the establishment of a chemical equilibrium with the capsule liner which results in a stable O/Pu stoichiometry so that no further oxidation would occur during subsequent aging from a fire or reentry condition.

As an integral and continuing part of the investigation of the compatibility between the T-111 liner and the plutonia, we wished to examine two facets of this problem, viz., 1) the measurement of the partial pressure of the oxygen in the capsule

during heat treatment, and 2) the measurement of the partial pressure of oxygen in the capsule during a subsequent heat-up which simulates either a fire or a possible reentry condition. These oxygen partial pressures had not been determined previously; the obtainment of these values will provide dynamic data regarding the effectiveness of the yttrium getter added to the fuel as opposed to estimating an optimum amount of yttrium, and the effect of the yttrium based upon metallographic examination of the fueled capsule after heat treatment.

An examination of the literature showed that the method of choice for studying the thermodynamics of this system would be the use of a solid oxide which functions as an electrolyte at high temperatures. This technique would also allow the free energy of formation of metal oxides of interest to be determined. Some free energies, for example that of hafnium oxide, have not been determined experimentally and this bears directly on the T-111 stability since hafnium is the oxygen getter in the alloy.

A secondary purpose of the present investigation was to examine techniques for studying the mechanisms by which oxygen and other gases react with the T-111 surface and thus to eventually obtain a comprehensive picture of both the thermodynamics and kinetics of the factors affecting the T-111 embrittlement.

The method of choice for the kinetic investigation was high-temperature Auger Electron Spectroscopy (AES). This approach is a highly exploratory one since it has not been demonstrated that the technique can function at the desired

temperature of investigation or that the results will be meaningful and therefore useful.

Experimental technique

Equipment

The electrolytic cell used for the present study is shown schematically in Figure 1. The cell consists of a 7-1/2 mole % yttria-doped thoria (YDT) tube that is attached to a cylinder of Macor* via high-temperature metal/glass solder. The machinability of the Macor permits metal fittings and other attachments to be made while maintaining the desired leak-tightness and integrity of the system. The Macor extension was provided so that the thoria tube could be sealed while the fittings providing the leak-tight seal were not exposed to the high temperatures of the furnace.

A Conax fitting on top of the Macor was epoxied in place and allowed a thermocouple, contained in an alumina sheath, to be inserted the length of the thoria tube so that it contacts a reference material placed inside of the thoria tube. The grooves machined on the outside of the Macor support two alumina sheaths, one of which accommodates a thermocouple and the other of which contains an iridium lead.

A mullite tube isolates the entire system via an O-ring face seal. The material to be studied, other than the T-111 container with $^{238}\text{PuO}_2$, is placed in a high-purity alumina thimble which is placed in the mullite tube in a manner similar

*Macor - Product of Corning, Inc.

FIGURE 1 - Schematic diagram of electrolytic cell and electrolytic cell assembly.

to the placement of the heat source capsule itself (MWG), which is shown in Figure 1. In the latter case the design is such that the thoria tube and the two alumina sheaths are press fits with the heat source capsule. In either case, the outer thermocouple and the iridium lead are touching or maintained in proximity to the thoria tube.

The system was assembled so that either the platinum or rhodium legs of the thermocouples could be used to measure the cell voltages after the EMF generated by the thermocouple-to-copper junctions was compensated by means of an ice bath. The digital voltmeter (DVM) and digital temperature meter (DTM) used for these measurements consisted of a Hewlett-Packard Model 3490A Multimeter and a Kiethly Digital Thermometer, Model 2100A,

respectively. The voltages and temperatures of interest could be obtained by switching to the appropriate points. The complete system arrangement is shown schematically in Figure 2.

A second cell was also used in some of the experiments. This cell consisted of a calcia-stabilized zirconia (CSZ) tube. This tube was sufficiently long, however, that a modified Cajon fitting with an O-ring face seal could be used in conjunction with a modified Conax fitting in order to access the interior thermocouple (TC) while maintaining a closed inside portion without need for the Macor extension. The arrangement of the thermocouples and the iridium lead was identical to the previously described configuration. Both types of cells were helium leak checked to 10^{-10} cm³/min before use.

FIGURE 2 - Diagram of thermodynamic system.

Materials

ThO_2 - 7-1/2 mole % $\text{YO}_{1.5}$ tubes, approximately 6 in. long x 1/4 in. o.d. x 1/8 in. i.d., and closed at one end were obtained from Zircoa Products, Corning Glass Works. Longer thoria tubes were not available commercially. This composition represents high-purity material which meets WADCO Specification S-618. The ZrO_2 tubes used were doped with 7-1/2 mole % CaO and were 10 in. long x 1/4 in. o.d. x 3/16 in. i.d.

The reference material was prepared by mixing 85 wt % chromium metal (99.95% min.) with Cr_2O_3 (99.999 % min.). The metal/metal oxide systems studied were prepared in a similar manner using materials of 99.98% minimum purity or better.

The $^{238}\text{PuO}_2$ studied was heat-source-grade material obtained by the standard Mound process.

Procedure

With the exception of the specimen for the partial oxygen pressure measurement in the T-111 capsule fueled with $^{238}\text{PuO}_2$, the materials to be studied were loaded into a high-purity alumina thimble. This thimble, along with the cell and its auxiliary components, was transferred to an inert box where the final assembly took place. This inert box was argon-filled and typically showed an oxygen concentration of less than 5 ppm. The oxygen concentration in the alpha box where the $^{238}\text{PuO}_2$ experiments were performed was maintained at less than 1 ppm during the course of the experiments by recirculating the atmosphere through an oxygen getter.

Before any cell measurements were taken on the metal/metal oxide systems studied, the cell was conditioned at about 500°C for several days and then run up to high temperature - typically the upper temperature of the expected operating range. The cell temperature was then lowered to the desired initial temperature and equilibrium was obtained before measurements were performed.

The criterion for acceptance of cell measurement readings was that the measured cell voltages should repeat at a temperature of interest as the furnace temperature was varied above and below this temperature, while allowing equilibrium to be attained between readings. In addition, we felt that the readings should be repeatable on a between-day basis, which was found to be the case within $\pm 2\text{mV}$. In this manner each measured point represents between six and eight measurements at a given temperature both within and between days.

Results and discussion

Measurement of free energies of formation of tantalum and hafnium oxides

The following four cells were used in this portion of the work, all of which were coexistence electrodes with two condensed phases:

- (I) $\text{Pt}|\text{Ta}, \text{Ta}_2\text{O}_5|\text{Th}_{0.85}\text{Y}_{0.15}\text{O}_{1.925}|\text{Cr}, \text{Cr}_2\text{O}_3|\text{Pt}$
- (II) $\text{Pt}|\text{Ta}, \text{Ta}_2\text{O}_5|\text{Zr}_{0.85}\text{Ca}_{0.15}\text{O}_{1.85}|\text{Cr}, \text{Cr}_2\text{O}_3|\text{Pt}$
- (III) $\text{Pt}|\text{Hf}, \text{HfO}_2|\text{Th}_{0.85}\text{Y}_{0.15}\text{O}_{1.925}|\text{Cr}, \text{Cr}_2\text{O}_3|\text{Pt}$
- (IV) $\text{Pt}|\text{Hf}, \text{HfO}_2|\text{Zr}_{0.85}\text{Ca}_{0.15}\text{O}_{1.85}|\text{Cr}, \text{Cr}_2\text{O}_3|\text{Pt}$

Since Ta_2O_5 and Cr_2O_3 are stable and relatively inert oxides, and free energies of formation are available in the temperature ranges of interest, Cell I was used to establish validity of the experimental procedure and to determine whether or not the previous temperature ranges of measurement could be extended. The value for the Gibbs free energy of formation of the Cr/Cr_2O_3 system, used as the reference in this work, was that reported by Mazandarany and Pehlke [16]. These investigators reported $\Delta G^\circ_f(Cr_2O_3) = -266600 + 59.78T$ (cal/mole) (1150-1540 K), which agrees closely with previous studies [17-20].

The results of the present work [$\Delta G^\circ_f(Ta_2O_5)$] show excellent agreement with those of previous investigations [21-23]. The present results are graphically compared with previous investigations in Figure 3. The temperature ranges of measurement are also indicated.

Because of the future unavailability of the YDT tubes, these measurements were repeated using CSZ as the solid electrolyte in order to establish a comparison of the two materials. We would normally expect lower results because of the onset of electronic conduction at lower oxygen pressures. It has been estimated that ThO_2 -based electrolytes are useful to oxygen pressures three to five orders of magnitude lower than for ZrO_2 -based electrolytes [24]. For an ionic transfer number greater than 0.99, YDT will enable measurements to approximately 10^{-25} atm while ZrO_2 gives a lower limit of about 10^{-15} atm [25].

However, Patterson [26] has pointed out that the data on the electrolyte behavior of CSZ are becoming more abundant and that the onset of electronic conduction in CSZ at 1000°C occurs at about $3-8 \times 10^{-13}$ atm P_{O_2} or about down to Cr, Cr_2O_3 equilibrium coexistence.

FIGURE 3 - Free energy of formation of Ta_2O_5 using Cell I.

The results of using CSZ as the solid electrolyte using Cell II are shown graphically in Figure 4. These values average about 35 kcal/mole lower than those obtained with the YDT electrolyte. However, these $\Delta G^\circ_f(\text{Ta}_2\text{O}_5)$ values are similar to those determined by Matsushita and Goto [27] which are also shown in Figure 4.

The $\Delta G^\circ_f(\text{HfO}_2)$ was then determined using both the YDT and the CSZ as electrolytes in Cell III and Cell IV configurations, respectively. These results are shown in Figures 5 and 6. Cell III followed the relationship $\text{EMF} = 0.65693 - 0.000217T(\text{K})$ (V) (1123-1623 K). It can be seen that the results using the CSZ electrolyte are again appreciably lower, by about 30

FIGURE 4 - Free energy of formation of Ta_2O_5 using Cell II.

FIGURE 5 - Free energy of formation of HfO_2 using Cell III.

FIGURE 6 - Free energy of formation of HfO_2 using Cell IV.

kcal/mole. This difference is about the same as was determined in the case of tantalum. This direct comparison indicates, as before, that the electronic contribution from the CSZ is having a large effect on the final results. However, since the absolute difference is about the same, it may be possible to employ the CSZ as an electrolyte and use the absolute difference as a correction factor.

There are no previous experimentally determined values available for the free energy of formation of hafnium oxide. The only ones available are those calculated values listed by Coughlin [28]. These values are appreciably higher (~45 kcal/mole), which is probably because they are based on enthalpy and entropy data, some of which are estimated.

It is interesting to note that, although these results show that the free energy of formation of hafnium oxide is greater than that of tantalum oxide per gram atom of oxygen (-70632 vs. -64323 cal/mole at 1623 K, respectively), the difference is not nearly as great as had been previously thought. This suggests that the ability of hafnium to strongly function as an oxygen getter may be largely determined by the kinetics, and the driving force (free energy) may play a lesser role, albeit an important one. Thus, kinetic studies seem to be of vital importance in understanding the compatibility of materials and the effect of oxygen on T-111.

Measurement of the oxygen partial pressure within the T-111 liner

After completion of the free-energy measurements, the equipment was moved from an inert-gas box to an alpha box in order that the T-111 liners could be loaded with plutonia and attached to the thorium tube.

The iridium (see Figure 1) was included as a separate lead because previous compatibility studies have shown that $^{238}\text{PuO}_2$ readily attacks platinum at high temperatures; therefore a second lead of iridium was utilized to ensure that the cell voltage could be measured even under worst-case conditions.

As before, $\text{Cr/Cr}_2\text{O}_3$ was used as the reference material in the thorium tube. The cell consisted of $\text{Pt} | ^{238}\text{PuO}_2, \text{Y, T-111} | \text{Th}_{0.85}\text{Y}_{0.15}\text{O}_{1.925} | \text{Cr, Cr}_2\text{O}_3 \text{ Pt}$ and the oxygen chemical potential of the left-hand side is given by $\mu_{\text{O}_2} = -nFE + \mu'_{\text{O}_2}$. The partial pressure of oxygen in the capsule is given by:

$$\begin{aligned}\Delta G &= -nFE = -RT \ln K \\ -nFE &= -RT \ln K \\ -nFE &= -RT \ln (P'_{\text{O}_2}/P''_{\text{O}_2})\end{aligned}$$

$$\text{But } RT \ln (P'_{\text{O}_2}) = (2/3)\Delta G^\circ_f(\text{Cr}_2\text{O}_3)$$

$$\text{Therefore } \log (P''_{\text{O}_2}) = \frac{2[(1/3)\Delta G^\circ_f(\text{Cr}_2\text{O}_3) - 2FE]}{1.987 \times 2.303 \times T}$$

After $^{238}\text{PuO}_2$ fuel is loaded into the T-111 liner the radioisotopic heat source cover is welded onto the body, and the

Table 1 - PARTIAL PRESSURE OF OXYGEN IN MWG DURING HEAT-UP

Temperature (°C)	Time (min:sec)	$^{238}\text{PuO}_2$ without Yttrium (log P' O_2) ^a	Time (min:sec)	$^{238}\text{PuO}_2$ without Yttrium (log P" O_2)	Time (min:sec)	$^{238}\text{PuO}_2$ with Yttrium (log P" O_2)
Ambient	0	--	0		0	
750		-27.5	4:00	-27.4	2:33	-29.7
800		--	--	-29.6	3:17	-28.3
850		-28.7	5:35	-28.0	4:33	-27.2
900		--	--	-26.8	5:55	-25.9
950		-26.1	7:45	-25.1	6:24	-24.5
1000		-25.1	8:35	-23.6	7:19	-23.4
1050		-24.0	9:20	-22.4	8:12	-22.1
1100		-22.8	10:20	-21.3	8:33	-21.0
1150		-21.7	11:17	-20.2	10:05	-20.0
1200		-20.7	12:22	-19.2	10:57	-18.9
1250	6:12	-19.6	13:15	-18.4	12:38	-18.0
1300	9:00	-18.5	14:53	-17.6	14:07	-17.1
1350	12:27	-17.1	16:25	-16.9	15:40	-16.2
1400	13:00	-16.1				

^aPressures are in atmospheres.

capsule is brought up to 1350°C within 15 min and held at this temperature for 1 hr. The purpose of the heat treatment is to force an "in-situ" reaction that results in the establishment of a stable equilibrium in the capsule by virtue of the gettering action of the yttrium present in the $^{238}\text{PuO}_2$ charge, which results in a more stable fuel stoichiometry [15,29].

For the present study, separate charges of $^{238}\text{PuO}_2$ with and without yttrium were utilized so that direct comparisons could be made. The results of the oxygen partial pressure measurement during the initial heatup are shown in Table 1. These results show that there are no major differences in oxygen concentration between $^{238}\text{PuO}_2$ which contains yttrium and that which does not. The most obvious

effect is that the repeatable oxygen pressures indicate that any oxidation occurring is relatively slow. In fact, since the partial pressure of oxygen of Ta/Ta₂O₅ at 1000°C is 10⁻²⁵ atm, we would expect, in general, that the oxygen partial pressure in the capsule would be lower than measured as a result of the attack of the T-111, or that the fuel stoichiometry is such that during the heat-up period the O/Pu ratio is maintained at about 1.90 which corresponds to the partial pressures observed [30,31].

During one of the subsequent experimental runs when the $^{238}\text{PuO}_2$ charge was held at 1350°C for 1 hr, the cell voltage excursioned to almost 1 V in the reverse condition. It was later observed that the mullite outer tube had cracked, allowing

Table 2 - PARTIAL PRESSURE OF OXYGEN IN HEAT SOURCE DURING HEAT TREATMENT

Time (min:sec)	²³⁸ PuO ₂ without Yttrium		²³⁸ PuO ₂ with Yttrium	
	Temperature (°C)	(log P"O ₂) ^a	Temperature (°C)	(log P"O ₂)
0	1339.7	-16.6	1350	-16.2
5:00	1346.6	-16.5	1351	-15.7
10:00	1354.2	-16.4	1355.8	-15.8
15:00	1355.1	-16.3	1354.8	-16.4
20:00	1350.6	-16.4	1355.1	-16.7
25:00	1351.9	-16.4	1353.6	-16.9
30:00	1351.0	-16.5	1355	-16.9
35:00	1350.0	-16.5	1356.1	-16.9
40:00	1349.5	-16.6	1355.4	-16.8
45:00	1351.3	-16.6	1356.1	-16.8
50:00	1351.5	-16.6	1357.4	-16.8
55:00	1350.7	-16.6	1350.2	-16.9
60:00	1239.8	-16.7	1347.2	-16.9

^aPressures are in atmospheres.

oxygen to enter the system during the time the oxygen gettering furnace was coming up to temperature. Since this compromised the remainder of the experiment, these results could not be included and a second charge of ²³⁸PuO₂ without yttrium had to be run.

The system was loaded and closed when the oxygen concentration in the alpha box was less than 1 ppm and the oxygen gettering furnace was brought up to temperature at the beginning of each run to maintain this condition during the run. In this manner, any minute leaks in the closed system would not contribute to error.

The oxygen partial pressures within the milliwatt generator heat sources during the 1-hr heat treatments are listed in Table 2. While there are no major differences between the oxygen partial

pressures with and without yttrium, the ²³⁸PuO₂ charge with yttrium shows consistently slightly lower results, which indicates that the yttrium is functioning in its designed role as a getter. These results are consistent with about what we would expect since low oxygen levels are maintained in both cases: oxygen reaction with the T-111 (tantalum) in one instance and oxygen reaction with the yttrium in the second instance. The ²³⁸PuO_{2-x} stoichiometry now appears to be dropping to the 1.85 O/Pu level.

The last portion of the experiment consisted in raising the temperature from ambient to 1350°C to simulate exposure of the sample to a fire or reentry conditions while measuring the partial pressure of the oxygen during this time period. A high oxygen pressure would indicate a good possibility of capsule embrittlement resulting from the interstitial

Table 3 - PARTIAL PRESSURE OF OXYGEN IN HEAT SOURCE
DURING SUBSEQUENT HEAT-UP (FIRE OR REENTRY SIMULATION)

Temperature (°C)	²³⁸ PuO ₂ without Yttrium		²³⁸ PuO ₂ with Yttrium	
	Real Time (hr:min)	(log P ["] O ₂) ^a	Real Time (hr:min)	(log P ["] O ₂)
750	--	-30.3	10:38	-39.3
800	--	-29.1	10:40	-33.2
850	1:32	-27.8	10:43	-29.6
900	--	-26.3	10:46	-27.5
950	1:42	-24.9	10:48	-26.5
1000	--	-23.6	10:52	-25.6
1050	1:50	-22.5	10:54	-24.6
1100	--	-21.4	10:57	-23.6
1150	--	-20.3	11:02	-21.9
1200	--	-19.4	11:05	-20.7
1250	--	--	11:09	-19.7
1300	--	--	11:11	-18.8
1350	--	--	11:14	-18.4

^aPressures are in atmospheres.

hardening described previously, which could cause capsule rupture in the event of an impact.

The results of this experiment are listed in Table 3 and show that the ²³⁸PuO₂ containing the yttrium produces a lower partial pressure of oxygen in the capsule. This indicates that the yttrium is indeed serving as an effective getter. In fact, the measured oxygen partial pressure corresponds closely with that measured for an O/Pu ratio of 1.78, as can be seen from Figure 7 which was reported by Kent [30]. It is interesting to note that an O/Pu ratio of 1.75 has been the target ratio based upon empirical data since the oxygen partial pressure has not been measured previously.

Figure 8 provides dramatic evidence of the importance of the O/Pu ratio in optimizing

the oxygen-tantalum reaction stoichiometry. As the O/Pu ratio becomes less, the partial molar free energy of oxygen of the PuO_{2-x} decreases and the stability of the plutonium oxide increases. These plots show that the ²³⁸PuO_{1.75} would be stable with respect to Ta/Ta₂O₅. In fact, at this point oxygen would be transferred from the Ta/Ta₂O₅ to the fuel.

Kinetic studies

It has been previously demonstrated that the surface concentration of a component of interest in a binary ideal solution can be estimated from

$$\frac{x_1^S}{x_2^S} = \frac{x_1^B}{x_2^B} \exp \left(\frac{\gamma_2 - \gamma_1}{RT} \right) a$$

where: x_1, x_2 = surface (S) and bulk (B) molar concentrations of components 1 and 2, respectively

FIGURE 7 - Calculated partial pressures at 1440°C (1713 K).

FIGURE 8 - Partial molar free energy of oxygen for the $\text{PuO}_{2.00}$ - $\text{PuO}_{1.65}$ region as a function of temperature.

γ_2 = surface tension of component 2
 γ_1 = surface tension of component 1
 a = area (cm^2/mole)
 R = gas constant
 T = absolute temperature

Using the above equation, it was estimated that the hafnium concentration on the surface should be enriched several thousand times.

Previous studies of T-111 at different temperatures and oxygen pressures showed that the oxidizing rate was not sensitive to temperature between 1089 and 1473 K but was proportional to oxygen pressure and inversely proportional to the specimen thickness [8], which suggested that the rate-controlling step in internal oxidation is the gas-metal interaction at the surface.

In view of the calculated enrichment of hafnium on the surface and the close (albeit higher) affinity of hafnium for oxygen over tantalum, the question arises as to whether or not the oxygen is chemisorbed on the surface and then diffuses into the bulk or reacts preferentially with the hafnium, the oxide of which then diffuses into the bulk. While this question cannot be answered without a number of oxygen exposures at elevated temperatures, the single goal of this program was to determine whether or not the species on the surface and their concentrations could be measured.

Accordingly, the apparatus shown in Figure 9 was fabricated from molybdenum sleeving and Mo/Re wire. Disks of T-111 approximately 1/8 in. in diameter were

recrystallized for 1 hr at 1426°C and swaged into the molybdenum sleeves. The apparatus was loaded into the Auger spectrometer and programmed from ambient to elevated temperatures.

Figures 10 and 11 show that the hafnium surface concentration increases as a function of temperature. This is shown dramatically in Figure 12 which is an isothermal time plot of Hf/Ta and O/Hf ratios. A series of curves at different temperatures would provide the rate data needed to construct Arrhenius plots from which the activation energy and other relevant data could be extracted.

It can be observed that the initial oxygen-to-hafnium ratio is lower at the start than it is after the sample has reached temperature. The reason for this condition is not understood at this time.

Conclusions

The measurement of the oxygen partial pressure in the capsule has demonstrated that:

- a. Repeatable oxygen pressure in the capsule during pretreatment indicates relatively slow oxidation of T-111 in the MWG capsule during this cycle and/or constant fuel stoichiometry of approximately 1.90 O/Pu.
- b. The $^{238}\text{PuO}_2$ charges with yttrium show consistently lower oxygen levels through most of the temperature range of interest, indicating that the yttrium is functioning in its designed role as a getter.

End view showing T-111 sample in place

Side view of Mo sleeve

FIGURE 9 - High-temperature Auger holder.

FIGURE 10 - AES spectrum of sputtered clean surface of recrystallized T-111 at room temperature.

FIGURE 11 - AES spectrum of sputtered clean surface of recrystallized T-111 at 1266°C.

FIGURE 12 - AES relative response at ~1150-1200°C as a function of time.

c. The lower oxygen pressure in the capsule on subsequent reheating indicates yttrium is stabilizing at an O/Pu ratio of 1.75.

d. The O/Pu ratio of 1.75 is consistent with an enhanced stability of the PuO_{2-x} and, therefore, less reactivity with the T-111 and good compatibility.

The free energy of formation of hafnium oxide has been measured. Although the value is slightly more negative than that of the tantalum oxide per gram atom of oxygen, both are indeed very close.

The preliminary high-temperature Auger Spectroscopy work has demonstrated that:

- a. Surface species enrichment can be observed as a function of temperature.
- b. It should be possible to establish rate plots and activation energies for a given species.
- c. Basic information and techniques developed might provide methods for optimizing surface treatment and understanding the mechanism by which oxygen enters the bulk of T-111.

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References

1. Fromm, E., and H. Jehn, Metall. Trans., 3, 1685 (1972).
2. Hroz, G., Metall. Trans., 3, 3069 (1972).
3. Inouye, H., Refractory Metal Alloys, I. Machlin, R. T. Begley and E. D. Weisert (ed.), Plenum, New York, New York, 1968, pp. 165-195.
4. Ketchum, M. D., and C. A. Barrett, Contamination of Refractory Metals by Oxygen, Water Vapor, and Carbon Monoxide, NASA-CR-1537, General Electric Co. (May 1970), 129 pp.
5. Orwan, E., Symposium on Internal Stresses in Metals and Alloys, Institute of Metals, London, England, 1948.
6. Ansell, G. S., "The Mechanism of Dispersion Strengthening: A Review," in Oxidation Dispersion Strengthening, Proceedings of a Symposium Held at Bolton Landing, New York, June 1966, Gordon and Breach, New York, New York, 1968, pp. 61-141.
7. Ashby, M. F., Philos. Mag., 14, 1157 (1966).
8. Lin, C. T., H. Inouye and R. W. Carpenter, Metall. Trans., 4, 1839 (1973).
9. Bonesteel, R. M., D. J. Rowcliffe and T. E. Tietz, "Mechanical Properties and Structure of Internally Oxidized Niobium-1% Zirconium Alloy," in Proc. Int. Conf. Strength Metals Alloys 1967, 9, 597 (1968).

10. Hobson, D. O., "Aging Phenomena in Columbium-Base Alloys," in High Temperature Materials, Interscience, New York, New York, 1963, pp. 325-334.
11. Taylor, A., and N. J. Doyle, J. Less-Common Metals, 13, 33 (1967).
12. Etter, D. E., and W. H. Smith, J. Less-Common Metals, 27, 109 (1972).
13. Selle, J. E., and B. R. Kokenge, "Radioisotopic Fuel Capsule," U.S. Patent 3,659,107 (April 1972).
14. Lin, C. T., H. Inouye and R. W. Carpenter, Mechanical Properties and Structure of Oxygen-Doped Tantalum-Base Alloy, ORNL-4839, Oak Ridge National Laboratory, Oak Ridge, Tennessee (December 1972).
15. Teaney, P. E., and R. L. Wise, in Microstructural Science, Vol. 5, J. D. Braun, H. W. Arrowsmith and J. L. McCall (ed.), Elsevier North-Holland, Inc., 1977, pp. 425-441.
16. Mazandarany, F. N., and R. D. Pehlke, J. Electrochem. Soc., 121, 711 (1974).
17. Jeannin, Y., C. Mannerskantz and F. D. Richardson, Trans. AIME, 227, 300 (1963).
18. Tretjakov, V. J. D., and H. Schmalzreid, Z. Elektrochem., 69, 396 (1965).
19. Pugliese, L. A., and G. R. Fitterer, Metall. Trans., 1, 1997 (1970).
20. Coughlin, J. P., U.S. Bur. Mines Bull., 542, 68 (1954).
21. Ignatowicz, S., and M. W. Davies, J. Less-Common Metals, 15, 100 (1968).
22. Worrell, W. L., Thermodynamics, Vol. I, International Atomic Energy Agency, Vienna, Austria, 1966, p. 131.
23. Rapp, R., Ohio State University, Private communication to D. J. David, 1979.
24. Etsell, T. H., and S. N. Flengas, Chem. Revs., 70, 339 (1969).
25. Steele, B. C. H., and C. B. Alcock, Trans. AIME, 233, 1359 (1965).
26. Patterson, J. W., J. Electrochem. Soc., 118, 1033 (1971).
27. Matsushita, Y., and K. Goto, Thermodynamics, Vol. I, International Atomic Energy Agency, Vienna, Austria, 1966, p. 111.
28. Coughlin, J. P., U.S. Bur. Mines Bull., 542, 22 (1954).
29. Jones, G. J., J. E. Selle and P. E. Teaney, "Radioisotopic Heat Source," U.S. Patent 3,909,617 (Sept. 30, 1975).
30. Kent, R. A., Thermodynamic Analysis of MHW Space Electric Power Generator, LA-5202-MS, Los Alamos Scientific Laboratory, Los Alamos, New Mexico (March 1973), 108 pp.
31. Atlas, L. M., and G. J. Schlehman, Thermodynamics, Vol. II, International Atomic Energy Agency, Vienna, Austria, 1966, p. 407.

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