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Progress Report

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Flight-Systems-Safety Program

May 1982

Los Alamos Los Alamos National Laboratory
Los Alamos, New Mexico 87545

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Compiled by
S. E. Bronisz

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FLIGHT SYSTEMS SAFETY PROGRAM

May 1982

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ABSTRACT

This technical monthly report covers studies related to the use of $^{238}\text{PuO}_2$ in radioisotope power systems carried out for the Office of Space Nuclear Projects of the US Department of Energy by Los Alamos National Laboratory. Most of the studies discussed here are ongoing. Results and conclusions described may change as the work continues.

I. GENERAL-PURPOSE HEAT SOURCE (GPHS)

A. Impact Tests

The four fueled clads to be used in the DIT-3 impact test, received on May 25, 1982, are being characterized before the start of the 30-day aging treatment.

B. Iridium Welding (F. W. Schonfeld)

Gas porosity revealed by light and electron microscopy in the weld samples of several DIT-1 and DIT-2 capsules was documented in previous monthly reports.^{1,2} The fact that these cavities have been observed in "as-polished" sections shows that they are actual voids rather than etching artifacts, and their locations both within and adjacent to the weld bead suggest that they are produced by the physical and/or chemical changes that accompany the welding process. Obviously, voids in the grain boundaries of unaltered alloy near but not in the fusion zone indicate that fusion is not necessary for void production but that bringing the metal to a high temperature is necessary. When we consider reactions that might produce gases at temperatures below but near

the melting point of the iridium alloy, a number of possibilities are evident. For example, iridium dioxide and sesquioxide disproportionate in vacuum at temperatures exceeding $\sim 800^\circ\text{C}$ and produce oxygen and iridium trioxide.³ The oxygen pressure over the solid dioxide reaches 1 atm at $\sim 1100^\circ\text{C}$, and at low oxygen pressures (>1 atm), the dioxide vaporizes at temperatures $>1500^\circ\text{C}$.³ Thus, generation of significant local pressures seems possible as temperatures approach the melting temperature of iridium. Because of the propensity of all platinum-group metals to absorb hydrogen and oxygen,⁴ another source of gas might be found in the reaction of hydrogen and/or oxygen with other impurities, such as carbon. Carbon is, in fact, an attractive candidate for one of the reactants for several reasons.

1. Carbon is soluble in molten iridium but essentially insoluble in solid iridium.^{5,6} (A test button prepared by adding carbon to DOP-26 alloy shows that the presence of tungsten and thorium does not alter these characteristics.)

2. Carbon does not interact with iridium (or the DOP-26 alloy additions) to form intermediate phases but precipitates as graphite flakes during eutectic solidification.

3. These phase relationships ensure that carbon present in the molten alloy will be rejected to grain boundaries during solidification, and the lack of solid solubility means that the graphite flakes usually will remain associated with the grain boundaries, even when subjected to rolling, forming, and heat treatment.

4. When exposed to oxygen (or perhaps hydrogen) at high temperatures, the small graphite flakes convert rapidly to CO or CO₂ (or one or more hydrocarbons) that could exert sufficient pressure on the solid to produce the voids.

A small extension of the same postulate will help explain the "quench-taper, internal centerline cracking" phenomenon. The presence of cracks in the first-pass weld metal at the early part of the taper-down, at weld bead edges, and at the taper-down of separate vent holes (Savannah River Plant experience) suggests that crack and void formation require the same conditions, namely, a temperature approaching the melting point of the bulk alloy. A reasonable first assumption is that the cracking results from a "hot-short" condition caused by segregation of enough eutectic component to produce a liquid film that cannot support stress. The "ridge networks," first observed by W. C. Mosely, Savannah River Laboratory (SRL), support the hot-short postulate. Our recently improved scanning electron microscopic capacity has provided additional information that reveals the existence of a typical eutectic structure on some crack surfaces. The photomicrograph of Fig. 1 illustrates this point.

However, photographic evidence of the existence of an eutectic mixture provides no clue to its elemental composition. For direct analyses, the Auger Electron Spectroscopy (AES) technique is very useful when investigating thin films on grain faces, etc., and essentially all of our pertinent analytical data come from that source. These data, and those of SRL and Oak Ridge National Laboratory (listed in SRL reports DPST-810128-2⁷ and SPST-81-128-3⁸), suggest that thorium does indeed segregate to the grain boundaries of the alloy in both the cast and wrought conditions. As anticipated, segregation is more extreme in the cast material (weld bead). The actual concentrations, however, are quite variable and no consistent and detailed pattern is evident. Fairly often, AES peaks attributable to carbon and oxygen have been observed at Los Alamos, but these indications were viewed with skepticism for two reasons. 1) The AES vacuum chamber contains residual amounts of oxygen and hydrocarbons that can be adsorbed on the specimen surface (long-term exposures of specimens in the AES

instrument showed significant increases in carbon and oxygen peak heights), and 2) sputtering can sometimes create "clouds" or "plumes" of removed materials that can redeposit on the specimen surface. There was no reason to question the practice of discounting the carbon and oxygen peaks until the weld-crack problem appeared. AES analyst S. Kosiewicz (Los Alamos, CHM-1) carried out a simple test in which he measured the rates of increase of the carbon and oxygen peaks with time. He concluded that these rates are sufficiently low in his instrument that analyses made for those elements in the first 30 min after specimen fracture should be considered valid. This change of viewpoint makes necessary a re-examination of the possible impurity effects of weld cracking. Conversion of the low-level and impurity elements in the alloy from weight to atomic concentrations adds clarity to comparisons of their effects on phase relationships. The 60 ppm (weight) of thorium in a binary iridium-thorium alloy is about 50 ppm (atomic) or 0.005 at.%, whereas 35 ppm (weight) of carbon in a binary iridium-carbon mixture is equal to 560 ppm (atomic) or 0.056 at.%, and 50 ppm (weight) of oxygen in iridium is equal to 600 ppm (atomic) or 0.06 at.%. In a DOP-26 alloy that meets specifications, we can have atomic concentrations of both carbon and oxygen that are more than 10 times the thorium content.

The phase relationships must be examined before we can determine potential interactions. The iridium-rich portion of the iridium-thorium diagram⁹ indicates that the eutectic point between iridium and Ir₃Th lies at 13 at.% thorium and 2080°C. The x-ray density¹⁰ of Ir₃Th is 18.88 kg/m³, and a good working value for the density of iridium is 22.6 kg/m³; thus, the relative volumes of the two phases in an equilibrium eutectic structure are 81 vol% Ir₃Th and 19 vol% iridium. If an iridium-thorium alloy contains 60 ppm (weight) of thorium, under equilibrium conditions, the relative amounts of Ir₃Th and the eutectic mixture are 0.037 and 0.045, respectively.

The data concerning the iridium-carbon phase diagram are fragmentary. The literature¹¹⁻¹³ states that no compounds exist and that carbon precipitates as flakes; it also reports two eutectic temperatures (2296 ± 16°C and 2110 ± 25°C). To establish a rough value for the eutectic composition, we made two alloy buttons by induction melting of 1) unalloyed iridium and 2) the DOP-26 alloy in high-purity graphite, holding the melt at 2500°C for about 30 s before cooling. The optical microstructures are shown in Fig. 2. To a first approximation, the two structures are so similar that we

(a) (b)
Fig. 1. The surface of the weld-overlap crack in IRG-80 showed a prominent ridge network and areas of eutectic structure (arrows); (a) 720X, (b) 2900X.

conclude that the presence of 0.3 wt% tungsten and 60 ppm thorium does not materially alter the microstructural features from those of the binary alloy. The structures confirm the literature statements as to the absence of intermediate phases and, in addition, illustrate that the preparation method does not provide equilibrium phase relationships. (The inductive stirring of molten iridium may erode graphite flakes from the crucible that cannot fully dissolve in the short time available, or the rapid cooling may depress the eutectic temperature so that graphite needles deplete the liquid of carbon to a hypoeutectic value.) However, because the welding process is itself a nonequilibrium process, these factors are of little importance.

The basic reasons for producing these alloys with carbon were 1) to obtain a reasonable estimate of the iridium-carbon eutectic compositions, 2) to make certain that this estimate is applicable to the DOP-26 alloy, and 3) to establish the general features of the eutectic morphology.

(a)

(b)

Fig. 2. Pure iridium (a) and the DOP-26 alloy (b) melted in graphite had closely similar microstructures, 250X.

Analyses of several sections from the melted buttons indicate that the effective iridium-carbon eutectic composition is 6-8 at.% carbon and that the DOP-26 alloying constituents (tungsten, thorium, and aluminum) do not affect that composition. Obviously, existing factors ensure that an accurate value for the eutectic composition cannot be obtained from these specimens of unknown total carbon content; lack of equilibration and the wide differences in polishing responses of the two phases are among the factors. The individual graphite flakes appear larger than they are because the polishing process abrades them faster and rounds off the edges of the resulting depressions.

Using 7 at.% as the probable composition, we can calculate the relative amount of liquid that might be present at $T_{eut} + \Delta T$. The amount for a binary iridium-carbon alloy that contains 35 ppm (weight) of carbon is 0.080 vol%, as contrasted to the 0.045 vol% for an equilibrium binary iridium alloy that contains 60 ppm (weight) of thorium. Because the 13-at.%-thorium composition for the eutectic is the equilibrium value, we have made a correction after examination of a 5-wt%-thorium arc-melted button that certainly experienced a rapid cooling rate. In this alloy the eutectic contains 65 vol% Ir_5Th rather than the 81 vol% calculated for 13 at.%, suggesting that rapid cooling has shifted the eutectic composition to ~ 10 at.%. If this correction is added, the relative volume of liquid formed in the thorium alloy

might be increased to 0.05 vol%. Thus, it seems, on the basis of relative concentrations and binary phase relationships, that carbon is at least as likely as thorium to be involved in hot-short behavior.

Other factors suggest the involvement of carbon (and oxygen) in the observed weld cracking. The welding processes (fusion and solidification) reduce the total grain boundary area by increasing the grain size and thus raise the carbon and thorium concentrations at the surfaces of the growing columnar grains.

Because the capsule walls extract the heat symmetrically and rapidly, tensile stresses across the full-penetration bead are limited to the level produced by differential thermal contraction of the solid, as the solidification shrinkage of a thin film of eutectic must be very small. But when penetration ceases to be complete during the power ramp-down, the first-pass weld metal that remains solid must expand against the restraint of the sidewalls, and upsetting and buckling can occur. Now both factors necessary for crack production, stress and molten grain boundary films, can be present in the unmelted thickness during cool-down. Whether a crack will form may depend upon the thorium and carbon levels, the extent of segregation in the first-pass bead, the grain orientation of the first-pass bead, and the degree of plastic deformation; but if a crack does form on the interior surface, the eutectic (binary or ternary) film would then be exposed to the internal atmosphere of the

capsule. This atmosphere must contain oxygen derived from the hot fuel. At temperatures approaching 2000°C, the reaction between small graphite flakes and oxygen might rapidly and effectively remove all trace of the exposed graphite flakes.

The iridium-tungsten solid solution phase of the binary iridium-carbon eutectic mixture tends to wet the adjacent iridium surfaces so that the mixture largely disappears from the microstructure, or it might, in some cases, join with the remnants of the primary iridium-rich solid solution that separated the eutectic colonies to form the residual ridge networks. Figure 3 illustrates this. Additionally, the mobility of carbon in molten iridium must be high, so that a thin film of iridium-carbon eutectic liquid might divorce during freezing to produce larger flakes (or aggregates of smaller flakes) on grain surfaces. Oxidation of such flakes or aggregates would simply leave depressions, perhaps like those seen between the ridges.

Specific information concerning the solubility of oxygen in iridium is not available, but general statements similar to that of McBryde,¹⁴ "Melting in an inert atmosphere such as argon eliminates the absorption of oxygen by the liquid metal, and results in castings freer of gas cavities . . .," appear in many places. Therefore, it seems reasonable to assume that the solubility of oxygen in molten iridium is significant and that there may be a smaller solubility in the solid, but some solid solubility is indicated by examination of feature surfaces of the two melts (iridium + carbon and DOP-26 + carbon) previously described.

Comparisons of a polished section and a polished and etched section showed (Fig. 4) many more vacant or partially vacant graphite sites after etching, suggesting some extreme form of local attack during etching. However, examinations of newly fractured surfaces of the same specimens provided proof that the etching procedure had nothing to do with the apparent enlargement of the graphite sites. The fracture surface (Fig. 5) clearly reveals that the iridium-carbon eutectic structure can be modified in a drastic and inhomogeneous manner during or after solidification. The morphologies of the vacant and partially filled second-phase sites are strongly reminiscent of those gas porosity sites previously observed and suggest that the same mechanism is responsible. We believe that the graphite is attacked by oxygen (and possibly hydrogen) to produce CO (and possibly a hydrocarbon) that expands the site and consumes some or all of the carbon, in the brief period of time following solidification when the temperature remains sufficiently high to provide high atomic mobility

Fig. 3. At higher magnification, the weld crack in IRG-80 shows ridges, eutectic colonies, and small spikes of iridium (arrow) thought to be remnants of the iridium-carbon eutectic after the graphite flakes were removed by oxidation, 17 000X.

and good matrix plasticity. Presumably, some interaction must occur in the liquid state; but the carbon activity in solution in molten iridium at the eutectic concentration must be low, whereas it must increase to unity as soon as it precipitates in elemental form. Unfortunately, we have no information on the constitutional relationships between iridium and carbon, oxygen, or hydrogen and so can only speculate as to mechanics.

It appears that the hot-short weld cracking problem in DOP-26 iridium alloy is produced by the ternary phase relationships of the iridium-carbon-thorium system. Tungsten has no importance in this phenomenon because its maximum concentration is greatly exceeded by its solubility in both liquid and solid alloy. The solidification sequence probably is as follows. The first solid rejected is the iridium-tungsten solid solution (SS), which grows dendritically while rejecting both carbon and thorium to the liquid. As the concentrations of carbon and thorium increase, the composition of the liquid intersects the binary eutectic valley. At this point, iridium-tungsten SS and carbon (graphite) are precipitated, but thorium is rejected to the remaining liquid until the composition reaches that of the ternary eutectic, at which point the small amount of liquid remaining freezes as a mixture of iridium-tungsten SS, carbon, and Ir_3Th . A schematic diagram of a portion of this hypothetical liquid surface is given in Fig. 6.

(a)

(b)

Fig. 4. Sections of iridium-carbon alloys show either filled carbon sites (a, as-polished, 5400X) or partially vacant sites (b, etched, 5000X).

The first weld pass produces enrichment of the carbon and thorium at grain boundaries in such a way that some portions of the intergranular material have the binary and ternary eutectic compositions. When the weld is complete, the down-ramp decreases the extent of penetration, and the completely molten zone no longer extends through the bead thickness. At this point, the (mostly) solid portion must deform plastically (upset) to accommodate its thermal expansion to the constraint imposed by the body of the capsule. As the thermal cycle reverses and cooling begins, the upset portion is stressed in tension, but the still-liquid grain boundary material of eutectic composition cannot support the stress and a crack opens.

The situation may be complicated and aggravated by oxidation of the carbon component of the eutectics by either oxygen in the alloy or by an external source. Although the greatest contribution of the oxidation phase may be to obscure the microstructural relationships, some cracks might be generated by the weakening of grain boundaries through void formation alone. In any case, the observed microstructures and the related chemistries can be adequately explained as resulting from selective oxidation of the binary eutectic leaving residual ridges, whereas the presence of Ir_3Th in the ternary eutectic tends to preserve a smaller area with a typical eutectic appearance, whether or not the carbon was removed by a gas-solid reaction.

Fig. 5. The fresh fracture surface of an iridium-carbon alloy exposed rounded cavities and vacant areas suggesting that graphite flakes were eliminated by a high-temperature reaction that produced gas pressures high enough to enlarge the original sites, 6300X.

C. Early Compatibility Test (D. Pavone)

The accumulated exposure time for this test assembly, as of June 1, 1982, was 2314 h. No evidence of vent plugging was observed during this report period. Thus far, two periods of 41 and 66 h have been observed in which the helium release rate was about 50% of the generation rate.

D. Safety Verification Tests (R. Zocher)

1. **Mass Simulants.** Iridium-clad UO_2 pellets with the same geometry as GPHS fueled clads will be used in the launch-pad-abort safety tests. Thirty-eight simulants that were welded were leak-tight, exhibited a markedly uniform exterior weld bead, and were a close approximation of the desired mass (Table I).

2. **Ablation.** The first six aeroshells for the Safety Verification Tests were machined to simulate ablation. On four aeroshells, 1.02 mm was removed from the exterior surfaces to simulate the ablation resulting from

Fig. 6. A schematic diagram of the liquidus surface of the quasi-ternary system $\text{Ir(W)} + \text{C} + \text{Th}$, as suggested by observed microstructures.

TABLE I. Characteristics of 38 Mass Simulants Welded at Los Alamos

Target mass	202.7 g
Clad mass	53.23 ± 1.01 g
As-welded mass	203.73 ± 2.77 g
Weld width, exterior	2.40 ± 0.02 mm (0.0945 ± 0.008 in.)
Welded leak rate	$1 \times 10^{-8} \text{ cm}^3\text{s}^{-1}$

an orbit-decay trajectory, and 1.68 mm was removed from the surfaces of the other two aeroshells to simulate the ablation resulting from a minimum-gamma reentry.

3. **Explosion Testing.** The first GPHS module (PAL-002) for the explosion tests at Sandia National Laboratories was completed and assembled (Fig. 7). Four mass simulants (IRG-115, -116, -117, and -118) were used in the assembly.

Fig. 7. The explosion test module (PAL-002) contains four iridium-clad UO_2 mass simulants.

II. LIGHT-WEIGHT RADIOISOTOPE HEATER UNIT (R. Tate)

The first overpressure test of the Light-Weight Radioisotopic Heater Unit (LWRHU) was conducted by Sandia National Laboratories at their Coyote Test Field. A sizable explosive charge was detonated at one end of a long steel shock tube; the pressure wave at the other end, where the LWRHU was mounted, was approximately the desired 13.8 MPa (2000 psi). Apparently, the LWRHU was stripped of its mounting holder and graphitic protection, but a silhouette obtained by flash radiography shows that the fuel capsule was undistorted by the overpressure. The capsule was not found downstream in the large sawdust trap and may have escaped through an opening in the concrete blocks defining the trap box.

III. MULTI-HUNDRED WATT (D. Pavone)

A. MHFT-76

This assembly was impacted in a simulated orbital-decay reentry mode following aging for 8820 h in vacuum at 1210°C (graphite). An intermittent crack

extending from the hoop region toward the back of the impacted clad and several small hoop cracks were observed.

Emission spectrographic analysis of a sample of the plutonia sphere showed the following elements to be present in amounts exceeding the detection limit.

	ppm		ppm
Ca	50	Si	6
Mn	1	Ta	100
Al	35	Cr	35
Ti	25	Ni	10
Fe	55	Ba	2

The phosphorus content of the plutonia, determined by a colorimetric procedure, was 15 ppm. The result agrees well with the pretest gamma-scan result of <20 ppm.

Analysis of the recovered graphite debris indicated a total plutonium content of 40.4 mg and a phosphorus content equivalent to 38 ppm.

Emission spectrographic analysis of samples of the iridium clad taken from each hemishell indicated the following elements to be present in amounts exceeding the detection limit.

	Hemi A	Hemi B
	(ppm)	(ppm)
Mg	3	3
Al	40	50
Si	100	100
Cr	25	25
Fe	30	300
Ni	150	150
Cu	5	5
Pt	10	10

The silicon content of these hemishells is higher than that observed in other assemblies of this test series except for MHFT-65, in which one of the hemishells had 200 ppm of silicon.

AES analysis results of fracture surfaces of the samples from each hemishell of the iridium clad are listed in Table II and summarized in Table III. The results indicate substantial thorium depletion, particularly at the interior edge, no phosphorus at any of the locations analyzed, and strong silicon grain-boundary segregation at three locations in one hemishell. Carbon and oxygen

TABLE II. Results of AES Analysis of MHFT-76

Specimen	Treatment	Location	Auger Intensity Ratios						
			Th _{6s} /Ir ₂₂₉	P ₁₂₀ /Ir ₂₂₉	C ₂₇₀ /Ir ₂₂₉	O ₅₁₀ /Ir ₂₁₉	Si ₉₂ /Ir ₂₂₉	S ₁₅₀ /Ir ₂₂₉	Th _{6s} /Ir ₅₄
MHFT-76-A1	8820 h	Edge inside	0.16	---	---	0.50	---	---	0.02
	1210°C	Center	0.27	---	---	---	0.98	---	0.03
	GIS ^a	Edge outside	0.15	---	Trace	0.56	0.71	---	0.02
MHFT-76-A2	8820 h	Edge inside	Trace	---	---	0.66	---	---	Trace
	1210°C	Center	0.16	---	---	---	---	---	0.02
	GIS	Edge outside	0.28	---	---	---	0.78	---	0.04
MHFT-76-B1	8820 h	Edge inside	Trace	---	0.77	0.50	---	0.06	0.03
	1210°C	Center	0.24	---	0.67	0.83	---	---	0.04
	GIS	Edge outside	0.27	---	0.59	1.14	---	---	Trace
MHFT-76-B2	8820 h	Edge inside	0.04	---	0.48	0.63	---	---	Trace
	1210°C	Center	0.24	---	0.70	0.79	---	---	0.02
	GIS	Edge outside	0.41	---	0.52	0.80	---	---	0.06

TABLE III. Summary of AES Results for MHFT-76

Location	Auger Intensity Ratios					
	Th _{6s} /Ir ₂₂₉	P ₁₂₀ /Ir ₂₂₉	C ₂₇₀ /Ir ₂₂₉	O ₅₁₀ /Ir ₂₂₉	Si ₉₂ /Ir ₂₂₉	S ₁₅₀ /Ir ₂₂₉
Edge inside	0.05	---	0.31	0.57	---	0.02
Center	0.26	---	0.34	0.41	0.25	---
Edge outside	0.26	---	0.28	0.63	0.37	---
Average	0.20	---	0.31	0.54	0.21	Trace

were observed consistently in one hemishell, but in the other, oxygen was observed in only two locations and only a trace of carbon was detected.

Metallographic examination of vent assembly cross sections confirmed the visual observation that large amounts of effusate were deposited on the exterior surface surrounding the vent hole. Photomicrographs (Fig. 8) illustrate the extent of intermetallic reaction product formation. Figure 8a indicates that, adjacent to the vent hole, approximately one-third the thickness of the clad has reacted. Figures 8b and 8c illustrate the nature of the intermetallic reaction products. The elements identified in Fig. 8b were iridium, silicon, and plutonium. The light-gray and medium-gray phases contained only iridium and silicon, but with differing concentrations of silicon. Isolated third-phase particles containing plutonium as well as iridium and silicon were observed in this section. Six phases were observed in the section shown in Fig. 8c. The major phases contained principally iridium and silicon. Other phases contained

iridium and titanium with a low concentration of silicon; iridium, silicon, and oxygen; iridium, silicon, plutonium, and oxygen; and iridium, silicon, and plutonium.

Figure 9 shows an as-polished cross section of the iridium clad located near the vent hole of one of the vent assemblies. In addition to a transverse crack, an irregularly shaped defect is present. An enlarged photomicrograph of this defect is shown in Fig. 9b, which reveals the deposition of a dark-gray nonmetallic material. Electron microprobe analysis showed this material to consist of silicon, calcium, and plutonium with smaller concentrations of aluminum and titanium. The occurrence of nonmetallic material of this composition in this location indicates that the defect is not an unusual fracture resulting from the impact test but, instead, is an existing defect of the iridium clad into which fuel sphere impurities were deposited during the aging treatment.

In addition to plutonia, four other metallic phases were deposited in the interstices of the iridium filter element. The elements observed in these phases are

(a)

(b)

(c)

Fig. 8. Intermetallic reaction products on the exterior of the iridium clad of MHFT-76. The major phases contain principally iridium and silicon; (a) 50X, (b) and (c) 250X.

(a)

(b)

Fig. 9. Metallographic cross sections illustrating a defect in the iridium clad of MHFT-76. The nonmetallic deposit contained calcium, silicon, plutonium, and oxygen with some aluminum and titanium; (a) 50X, (b) 500X.

- (a) cerium, iron, magnesium, and oxygen;
- (b) calcium, silicon, and oxygen;
- (c) silicon, calcium, and plutonium with magnesium, cerium, manganese, titanium, and oxygen; and
- (d) as (c) plus aluminum.

B. MHFT-71

Because of evidence of nonmetallic vent deposits containing chlorine in this test assembly, a plutonia sphere sample from MHFT-71 was analyzed for chlorine using a pyrohydrolysis method. For comparison, plutonia sphere samples from MHFT-73 and MHFT-76 were also analyzed. The results obtained are

- MFHT-71 - 8 ppm chlorine;
- MFHT-73 - 70 ppm chlorine; and
- MFHT-76 - 25 ppm chlorine.

The results are confusing in that higher chlorine concentrations were present in those fuel sphere assemblies that did not exhibit effects like those seen in MHFT-71. The emission spectrographic analysis of the plutonia sphere indicated relatively high concentrations of titanium and zirconium impurities. This suggests that the occurrence of a relatively high concentration of titanium together with chlorine is responsible for producing the effects observed in MHFT-71.

IV. HELIUM RELEASE (D. Peterson, J. Starzynski, J. Early)

The rate of helium released from each of three plutonia samples exposed to a 12°C/min temperature ramp was analyzed this month. The diffusion constant was calculated as a function of temperature by assuming simple diffusion. The samples studied in these experiments had been withdrawn from the GPHS fuel pellet GP-19, as had most of the samples exposed to faster pulses. In the current study, the temperature was maintained at 1600°C following each ramp until the helium signal dropped to background. These runs were designated 63, 64, and 65. The diffusion constant logarithm is plotted vs the reciprocal temperature for the three runs (Fig. 10). The plots are linear over selected temperature ranges, but the slope increases drastically above about 1150°C. Corresponding results were obtained in earlier studies.

The sample parameters, percentage of helium released, activation energy (E_a), and effective constants of dif-

Fig. 10. Temperature dependence of effective diffusion constant determined from helium release measurements of plutonia exposed to 12°C/min ramp.

fusion (D'_0) associated with the low- and high-temperature regions are shown in Table IV. The overlap between the two linear regions has been excluded from the current analysis but soon will be included in the model.

Apparently, two mechanisms of helium release dominate in definite temperature regions. At lower temperatures, below about 1150°C, the helium release has an associated activation energy of 45 ± 2 kcal/mol helium. At higher temperatures, up to at least 1600°C, helium release is described by an activation energy of 132 ± 3 kcal/mol. It is encouraging to compare the helium release behavior observed here in the PuO_2 with that previously measured for UO_2 . Lawrence¹⁵ emphasizes, in a review of fission gas behavior in UO_2 , that previous workers have observed sharp breaks in the $\log D'$ vs $1/T$ plots, with the activation energy 46 ± 1 kcal/mol at lower temperatures and 129 kcal/mol at higher temperatures. Recently, Reynolds and Burton¹⁶ concluded that uranium ion diffusion along grain boundaries in UO_2 would have activation energy of 131.6 ± 4.4 kcal/mol. It appears reasonable that helium could display an analogous temperature dependence for diffusion along the grain boundaries in plutonia.

TABLE IV. Details and Results of Helium Released During 12°C/min Heat Pulse

Run	Mass (g)	Age (yr)	He (%)	Low Temperature		High Temperature	
				E _a (kcal)	Log D' ₀ (s ⁻¹)	E _a (kcal)	Log D' ₀ (s ⁻¹)
63	1.235	1.662	96.1	44.5 ± 0.2	-0.073 ± 0.37	132.0 ± 1.0	12.417 ± 0.130
64	0.891	1.695	95.1	48.4 ± 0.2	-0.660 ± 0.045	139.6 ± 1.1	13.335 ± 0.138
65	0.134	1.795	89.2	45.0 ± 0.2	0.223 ± 0.40	116.8 ± 0.8	10.246 ± 0.105

A SRL plutonium pellet weighing 18 g was divided into 21 parts. One section was submitted for metallographic analysis, and the remaining pieces were subjected to selected temperature ramps during which the helium release rates were measured. This approach should enable further correlations of the helium release behavior with the fuel microstructure.

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