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**^{238}Pu FUEL FORM PROCESSES
FINAL REPORT**

JANUARY—SEPTEMBER, 1983

MASTER

W. C. MOSLEY AND D. H. TAYLOR

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**E. I. du Pont de Nemours & Co.
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Aiken, SC 29808**

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**^{238}Pu FUEL FORM PROCESSES
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W. C. MOSLEY AND D. H. TAYLOR

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Publication Date:

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The Blaine air permeability test has been successfully adapted to measuring surface areas of $^{238}\text{PuO}_2$ powders. Measurements of surface areas of various nonradioactive powders were in good agreement with BET measurements of the same powders. A modification of the Blaine technique was developed to permit using small samples. Surface area was shown to be a more sensitive index of differences among $^{238}\text{PuO}_2$ powders than particle mode size. No correlation between surface area and fracture tendency of the pellets was found for the feed lots and pellets tested.

Helium Release From $^{238}\text{PuO}_2$ 76

An operating temperature of 1200°C is probably near optimum with respect to minimizing helium damage in $^{238}\text{PuO}_2$. Temperatures above 1300°C can lead to significant pore agglomeration which could alter the impact behavior of $^{238}\text{PuO}_2$ pellets.

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FOREWORD

This report is the last of a series that has been issued to summarize progress in the Savannah River Laboratory ^{238}Pu Fuel Form Program. This program was supported primarily by the DOE Advanced Nuclear Systems and Projects Division (ANSPD).

Goals of the Savannah River Laboratory (SRL) program included providing technical support for the production of $^{238}\text{PuO}_2$ fuel forms in the Savannah River Plant's (SRP) Plutonium Fuel Form (PuFF) Facility. This part of the program included:

Demonstration of processes and techniques developed by the Los Alamos National Laboratory (LANL) for production at SRP. Information from the demonstration provided the technical data for technical standards and operating procedures.

Technical Support to assist plant startup and to ensure continuation of safe and efficient production of high-quality heat-source fuel.

Technical Assistance after startup to accommodate changes in product and product specifications, to assist user agencies in improving product performance, to assist SRP in making process improvements that increased efficiency and product reliability, and to adapt plant facilities for new products.

The above program goals have been met. Regular funded technical assistance has been terminated. Future assistance will be provided on an as-needed basis as requested by SRP.

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GENERAL-PURPOSE HEAT SOURCE (GPHS) PROCESS SUPPORT

ANALYTICAL STUDIES OF WELD-QUENCH CRACKING IN DOP-26 IRIIDIUM ALLOY CLAD VENT SET

Introduction and Summary

Underbead cracks occasionally occur in girth welds on DOP-26 iridium alloy clad vent sets (CVS) in the region where the gas tungsten arc is quenched.^{1,2} Weld-quench cracking severity is different for each batch of DOP-26 iridium alloy. Replacement of the two-pole arc oscillator on the welder with a four-pole arc-pattern shaper significantly reduced weld-quench cracking.

Grain surfaces in weld-quench cracks are characterized by ridge networks. These ridge networks were originally thought to be caused by grain boundary liquation. However, scanning electron microscopy and electron microprobe analysis showed that ridge networks constituted grain boundary cavities that are distinctly different from thorium-bearing eutectic patches that cause weld-metal cracking in iridium alloys doped with more than 100 ppm thorium. Gas porosity and high temperature creep have been identified as possible mechanisms that could produce grain boundary cavities that lead to cracking.^{2,3}

Several analytical techniques have been used to try to correlate weld-quench cracking with elemental distributions in DOP-26 iridium alloy. Electron microprobe analyses showed that ridges and cavities between ridges contained less than 0.1 weight percent thorium.¹ Carbon was detected by scanning Auger microprobe analysis on ridge and cavity surfaces but not on uncavitated grain surface.² Secondary ion mass spectrometry (SIMS) showed that thorium, calcium, carbon, aluminum and boron segregate in DOP-26 iridium alloy.⁴ In MER alloy that had high weld-quench cracking susceptibility, thorium was segregated to grain boundaries in both welded and unwelded alloy. In LR alloy that had low weld-quench cracking susceptibility, some of the thorium was present as particles within welded grains. Also, more carbon-bearing particles were detected in LR alloy than in MER alloy.

Additional SIMS analyses have been performed on specimens from CVS's T38 (LR alloy) and T39 (MER alloy) to determine elemental distributions in specific areas of the weld quench regions. Ion images showed that thorium, calcium, and aluminum are generally associated in particles in welded DOP-26 iridium alloy but are not associated in unwelded alloy. Also, grain boundaries near a weld-quench crack in CVS T39 appear to contain less thorium and calcium than those in other areas of the weld-quench regions. Surface contamination prevented imaging of distributions of gas-forming elements like hydrogen, carbon, oxygen and nitrogen.

SIMS Analyses

A specimen from quench T3 in CVS T39 (cup MER 5-7) that had a large weld-quench crack was prepared for SIMS analysis. The specimen of quench T1 in CVS T38 (cup LR 316-6) that had no weld-quench cracks was reanalyzed. Specimens were sectioned perpendicular to the weld and polished to reveal the following areas of interest: alloy welded twice, alloy welded once, and unwelded alloy. Analysis positions were selected to include these areas plus the interface between alloy welded once and twice, the heat-affected zone below this interface (where weld-quench cracks form), and the interface between welded and unwelded alloy. Ion images were recorded for WO^+ , Ca^+ , Al^+ , and ThO^+ using oxygen ion bombardment and for Ir^- , O^- , C^- , IrN^- , H^- , S^- , and P^- using cesium ion bombardment. Calcium, thorium, aluminum, phosphorus, sulfur and carbon could cause grain boundary liquation in DOP-26 iridium alloy. Gas porosity could be caused by carbon, hydrogen, oxygen and nitrogen. The major constituents in DOP-26 alloy, iridium and tungsten, served as reference elements. Analyses were performed with two Cameca IMS-3F ion microscopes at Charles Evans and Associates of San Mateo, California. SIMS techniques were described in a previous report.⁴

Figure 1 shows areas selected for SIMS analysis. Both specimens were analyzed first with oxygen ions and then with cesium ions. The order in which data were collected is indicated numerically for cesium ion bombardment (negative ions) and alphabetically for oxygen ion bombardment (positive ions). Figure 2 shows the specimens after analysis. Images recorded with cesium ion bombardment were easily correlated with distinguishing features in the alloy grain structure. It was not possible to make such correlations for the images recorded with oxygen bombardment because the smaller analysis areas lacked distinguishing features. However, the analyzed areas are probably close to the selected areas.

Positive Ion Images

Figure 3 shows distributions of aluminum, calcium, thorium and tungsten in analysis areas in quench T3 of CVS T39 and quench T1 of CVS T38. Dark spots correspond to elemental concentrations in

Figure 1. SIMS Specimens Before Analyses Showing Selected Areas

100 μ m

Quench T3 in cup MERS-7
CVS T39

Figure 2. SIMS Specimens After Analysis

Figure: 3 POSITIVE ION IMAGES OF WELD QUENCH AREAS IN DOP-26 IRIIDIUM ALLOY .

particles. Elemental concentrations in grain boundaries produce dark lines. Variations in brightness for individual grains are caused by their different crystallographic orientations. The WO^+ images reveal no inhomogeneities in tungsten distributions in either the MER or LR alloy although variations in tungsten concentrations on grains surfaces have been detected by electron microprobe analysis.

The "F" analysis areas correspond to unwelded alloy. Particles containing aluminum, calcium and thorium were detected in unwelded LR 316-6 alloy. The distinct differences in these images show that, in general, these elements are not associated. Some calcium-bearing particles correlate with thorium-bearing particles. Only one calcium-bearing particle was detected in unwelded MER 5-7 alloy and it is uncertain if it correlates with a thorium-bearing particle. No Al^+ image was recorded for unwelded MER 5-7 alloy. Thorium-bearing grain boundaries are much more distinct in unwelded MER 5-7 alloy than in LR 316-6 alloy.

Analysis areas at the weld edges are designated as "E". No aluminum inhomogeneities are apparent in either alloy. Some calcium-bearing particles are faintly visible in the Ca^+ image for LR 316-6 alloy but it is uncertain if they correlate with thorium-bearing particles. The calcium-bearing particles in MER 5-7 definitely correlate with some of the thorium-bearing particles within alloy grains. LR 316-6 alloy at the edge of the weld contains more thorium-bearing particles than unwelded alloy. Some thorium-bearing particles within grains are in linear arrays. Linear arrays of thorium-bearing particles are frequently detected on grain surfaces of welded DOP-26 alloy and it is conceivable that similar distributions occur within grains. Thorium-bearing grain boundaries are much more distinct in MER 5-7 alloy than in LR-316-6 alloy.

Ion images in the "D" areas are for alloy welded once but fairly distant from the quench where weld-quench cracks generally do not form. Ion images for MER 5-7 alloy show almost identical distributions of aluminum, calcium, and thorium within grains and at grain boundaries. In LR 316-6 alloy, calcium appears to be homogeneously distributed and faint inhomogeneities in aluminum and thorium within alloy grains do not seem to correlate.

The "A" areas correspond to alloy welded once near the weld centerline below the quench where weld-quench cracks generally form. Area "A" in MER 5-7 is within 200 m of a weld-quench crack. Almost identical Ca^+ and ThO^+ images show that calcium and thorium are associated in particles within grains. The Al^+ image was recorded under different conditions and may not correspond exactly to the area covered by the Ca^+ and ThO^+ images. However, a similar distribution of aluminum in particles within grains is apparent. No grain boundaries are evident in area "A" of the

MER 5-7 alloy. Ion images for area "A" in cup LR 316-6 are similar to those recorded in area "D". Calcium appears to be homogeneously distributed. Particle distributions of aluminum and thorium within grains do not appear to correlate.

The "B" areas are at the depth of penetration of the weld during quenching. Large weld-quench cracks, like the one in quench T3 on CVS 39, often penetrate through this area into the columnar grain region of the quench. Area "B" in cup MER 5-7 is within 200 μm of the crack. Almost identical Al^+ , Ca^+ , and ThO^+ images show that aluminum, calcium and thorium are associated in particles within grains. A grain boundary across area "B" contains practically no thorium and very little calcium and aluminum (Figure 4). Ion images for area "B" in cup LR 316-6 show only faint evidence of particles containing aluminum, calcium, and thorium within grains. It is not possible to determine elemental associations.

The "C" areas correspond to alloy welded twice during quenching of the gas-tungsten arc. Aluminum appears to be homogeneously distributed in both alloys. Thorium appears homogeneously distributed in LR 316-6 alloy but in MER 5-7 alloy it has segregated into particles within grains and on grain boundaries. In cup MER 5-7, thorium-bearing particles seem to be more finely dispersed in alloy welded twice than in unwelded alloy (area "F") and alloy welded once (areas "D" and "E"). Also, thorium-bearing grain boundaries are less distinct in alloy welded twice than in unwelded alloy and alloy welded once. Calcium-bearing particles are present in both alloys. In alloy MER 5-7, the calcium-bearing particles correlate with thorium-bearing particles.

Negative Ion Images

Images recorded with negative ions (Ir^- , O^- , C^- , IrN^- , P^- , S^- , and H^-) in selected areas of quench T3 of CVS T39 and quench T1 of CVS T38 are shown in Figures 4 and 5, respectively. In general, these images appear to correspond to contamination on the specimen surfaces rather than distributions of elements within the alloys. Most of the elemental indications occur as clusters of particles near the edge of the aperture rather than being distributed uniformly across the specimen surfaces. Particles containing oxygen, carbon, hydrogen, and nitrogen generally correlate and, thus, show the association of these elements which are atmospheric components. The amount of surface contamination decreases in the order in which the areas were analyzed. This order probably corresponds to increasing time of cesium ion bombardment.

1-1

IONS

Area Location

- 6 Unwelded
- 5 Edge of Weld
- 4 Welded Once
- 1/2 1 Welded Once (Near Centerline)
- 2 Edge of Quench
- 3 Welded Twice

100µm

Figure 4. SIMS ^{Negative} Ion Images for Quench T3 in CV5 T39 (MER5-7)

* No image recorded

Figure 5. SIMS Negative Ion Images for Quench T1 in CVS T38 (LR316-6)

Interpretation of SIMS Results

The SIMS results reported have extended our knowledge of the effects of gas-tungsten welding arc and quenching on DOP-26 alloys gained in previous studies. The present work confirms that welding redistributes aluminum, calcium, and thorium and that MER alloy (severe weld-quench cracking) and LR alloy (least weld-quench cracking) respond differently to welding. Aluminum, calcium and thorium are generally not associated in particles in unwelded MER and LR alloys. Welding of MER alloy caused the compounds containing these elements to react to produce particles (within grains and on grain boundaries) and grain boundary deposits in which aluminum, calcium, and thorium are associated. In contrast, welding LR alloy appears to homogenize aluminum, calcium and thorium. The faint indications of particles containing these elements in welded LR alloy fail to show that they are associated.

The present SIMS results suggest that weld-quench cracking may not be related to grain boundary deposits containing thorium and calcium. Ion images recorded for cup MER 5-7 show grain boundary concentrations of thorium and calcium to be lower near the weld-quench crack than in welded alloy away from the crack. This result is consistent with the observation that grain surfaces in weld-quench cracks are characterized by cavities in the form of ridge networks rather than extensive thorium-bearing deposits.

Contamination by atmospheric components prevented imaging of elements that could cause gas porosity. Previous analyses showed carbon to be distributed in particles in DOP-26 with LR 316-6 alloy having more carbon-bearing particles than MER 5-7 alloy.⁴ Knowledge of the distributions of gas-forming elements would be helpful in understanding weld-quench cracking. However, no further SIMS analyses are planned at this time.

IRIDIUM/ $^{238}\text{PuO}_2$ COMPATIBILITY TEST

Introduction and Summary

The Savannah River Plant (SRP) makes $^{238}\text{PuO}_2$ general purpose heat sources (GPHS) to power radioisotopic thermoelectric generators (RTG) for NASA deep space probes. After being fabricated into ceramic pellets approximately one-inch-long by one-inch in diameter, the PuO_2 is encapsulated in a 0.028-inch thick iridium shell which is vented on one end to permit escape of the decay helium. The purpose of the iridium shell, or clad vent set (CVS), is to provide long term containment of the plutonium dioxide and immobilization following an accidental re-entry impact. Safety verification impact tests (SVTs) of the capsules are performed at Los Alamos National Laboratory (LANL). In September 1979 a safety verification test of a fuel form of an earlier, spherical, design showed catastrophic failure of the iridium containment shell. Investigation of this failure by an interagency task force suggested that the failure was caused in part by small amounts of phosphorus on the grain boundaries of the iridium shell. Further study showed the PuO_2 fuel to be the primary source of phosphorus. The present study was undertaken in response to the findings of the task force. The work was performed jointly by personnel from Savannah River Laboratory (SRL), LANL, and Oak Ridge National Laboratory (ORNL) and had the following objectives.

- Assess the compatibility of the present chemical purity of the PuO_2 and the iridium alloy currently used to fabricate clad vent sets.
- Establish limits for phosphorus (P) concentration in the PuO_2 fuel so as to minimize phosphorus transport to the iridium cladding.
- Assess the effects of other major impurities in the fuel such as calcium (Ca), aluminum (Al), silicon (Si), and iron (Fe) on phosphorus transport.
- Assess the effects of these impurities on vent plugging and metallurgical properties of the iridium cladding.
- Assess the effectiveness of vacuum outgassing of the fuel in preventing vent plugging.

The overall results of this study indicate that the chemical purity of the fuel used presently to fabricate fueled clad vent sets will not present any special problems to the performance of the

fueled clad vent sets as intended. However cation impurities in the fuel can have a deleterious effect on the iridium cladding and vents and should be minimized as much as practical. Fueled capsules for which the PuO_2 has high Ca, Al, or Si content might enhance volatilization of material to the vents if they are stored at elevated temperatures for several months.

Other findings from the study are:

- The P concentration in the PuO_2 fuel should not exceed approximately 15 ppm to minimize transport of P into the Ir cladding. The effects of other major impurities on phosphorus transport could not be determined because the test did not compare fueled capsules having equivalent levels of P but different levels of the other impurities.
- The effects of the major impurities are to enhance Pu vaporization out of the CVS, enhance grain growth in the Ir cladding, and contribute to deposits in the vents.
- Vacuum outgassing as a final step may contribute to vent plugging.

Precise limits or specifications on impurities cannot be set based on the limited four capsule experiment. Any reduction of the impurity level will, however, improve the Ir/ PuO_2 compatibility.

Experimental Procedure

Four full-scale GPHS pellets (serial numbers 44, 45, 48, and 49) were made by SRL in the Plutonium Experimental Facility (PEF) using Technical Standard centerline fabrication conditions and standard $^{238}\text{PuO}_2$ feed powder. The test matrix is given in Table 1. Pellet 44 was made using standard conditions, including vacuum outgassing of the heat treated pellet and background (undoped) concentrations of phosphorus and other cationic impurities. Pellet 45, was identical to 44 but was not vacuum outgassed. (Feed for Pellet 45 was not from the same batch but was still standard feed.) Pellet 48 was considered a standard pellet, but was doped with 20 to 30 ppm phosphorus. Pellet 49 was doped with P, Ca, Al, Si, and Fe and fabricated in the standard way. The impurities were added by first slurrying the PuO_2 with a solution of H_3PO_4 and Na_2SiO_3 and evaporating to dryness. The powder was then slurried again in a solution of $\text{Al}(\text{NO}_3)_3$ and $\text{Ca}(\text{NO}_3)_2$ and evaporated to dryness. This technique for doping is standard in the ceramic industry. Fe was added as $\text{Fe}(\text{NO}_3)_3$. However, spark source mass spectroscopy (SSMS) showed that for all of the pellets in this test, the background concentration of Fe was so high that those pellets which had been doped with Fe could not be distinguished from those which had not. The source of this background Fe is not known.

TABLE 1

Test Matrix for Ir/PuO₂ Compatibility Test

Sample Number	SRL Run No.	Phosphorus Concentration	Cation Concentration		Vacuum Outgassing
			Ca, Al, Si	Fe	
1	44	Background (~5 ppm)	Background (30-50 ppm)	Background (~1000 ppm)	Yes
2	48	20-30 ppm	Background (50-200 ppm)	Background (~7000 ppm)	Yes
3	49	7-40 ppm	100-1000 ppm	Background (70-10,000 ppm)	Yes
4	45	Background (~4 ppm)	Background (50-200 ppm)	Background (800-2000 ppm)	No

A slice was cut from each heat treated or vacuum outgassed pellet prior to encapsulation for use as control specimens. Pre-aged metallography and chemical analysis was performed on these specimens. The remainder of each pellet was encapsulated by SRP in the Plutonium Fuel Form (PuFF) Facility using near flight quality type iridium cups and forwarded to LANL. At LANL the clad pellets were enclosed in two-pellet GPHS graphite impact shells (GIS's) made of FWPF-3D carbon-carbon-composite and prebaked to duplicate the condition of the flight hardware in order to simulate expected service conditions (temperature gradients, etc.). The samples were aged at LANL at RTG operating temperatures (Table 2). No re-entry thermal pulse was given the samples. After aging, the capsules were sectioned for chemical analysis and metallurgical characterization.

TABLE 2

Test Conditions

Aging temperature	GPHS-RTG iridium operating temperature - 1310°C (maximum fuel temperature approximately 1441°C)
Aging time	6 months
Aging atmosphere	Vacuum (about 1×10^{-6} torr)

The iridium cups used in the test were chosen to be as close to flight quality as possible. Cups used for Pellets 44 and 45 had numerous dye penetrant indications plus a grit blasted surface below the minimum requirement. Cups used for Pellets 48 and 49 had a wall thickness over maximum. Archive rings from each cup were used for control samples. Each ring was cut in half. One half was used to characterize the bulk and grain boundary chemistry and grain size in unaged iridium. The other half was used to characterize the iridium after aging at temperature but not in the presence of PuO_2 . Prior to any analyses, the archive rings were given a one-hour heat treatment at 1500°C in vacuum to provide them with the same thermal history as the iridium cups.

As an additional control, two unvented cups were welded together empty. The empty welded clad (designated T-40) was heated unfueled in a GIS. Because this clad had no vent, impurities could only be introduced into the iridium by diffusing in from the outside.

The orientation of the capsules during aging was indexed so that capsules could be sectioned in a manner that would allow observed features to be related to the aging position. The configuration of the capsules in their graphite fixtures during aging is shown in Figure 6.

The test conditions are given in Table 2.

Summary of Ir/ PuO_2 Compatibility Test Results

Effect of Aging on PuO_2 Fuel

PuO_2 Chemistry (Tables 3 through 5)

- The impurities of most concern are Si, Ca, Al, P, Mg (magnesium), Fe, Cr (chromium), Ti (titanium) (see Table 4 for current specifications).
- Both SSMS and electron microprobe analysis (MP) showed the above impurities to be inhomogeneously distributed in the PuO_2 . This inhomogeneity is both local (on grain boundaries rather than in solid solution for Ca, Si, Al) and regional (some regions of the pellets have higher concentrations than others). MP showed that iron and phosphorus were more homogeneously distributed on a local level. With the exception of Fe and Cr, changes in the bulk concentrations of the impurities during aging were less than the sensitivities of the analytical techniques used to measure them. Fe and Cr were reduced by up to two orders of magnitude during aging.

TABLE 3

Chemistry of PuO₂ Fuel Before and After Aging as Measured by
Spark Source Mass Spectroscopy (SSMS)

Concentration given in weight ppm.

Key to Table

Surf = Sample taken near pellet surface

Core = Sample taken from core region of pellet

H.T. = Pellet heat treated for 6 hours at 1525°C in oxygen

V/O = Pellet heat treated as above followed by vacuum outgassing for 1 hr at 1500°C

Aged = Pellet aged for 6 months in vacuum at about 1441°C (fuel temperature)

Element	44 Surf			44 Core			45 Surf		45 Core	
	H. T.	V/O	Aged	H. T.	V/O	Aged	H. T.	Aged	H. T.	Aged
Al	20	30	5	30	30	10	50	3	60	10
B			0.4			0.4		<0.01		<0.02
Ca	2	2	6	2	2	10	4	0.3	3	7
Cl			8			10		5		2
Co			2			0.7		<0.3		<0.2
Cr			70			20		20		10
Cu			4			2		2		0.7
Fe	1,000	1,000	300	900	900	100	800	100	2,000	70
K			0.4			0.8		0.7		0.05
Mg			1			1		0.7		0.5
Mn			30			10		5		8
Mo			4			3		1		0.5
Na			1			1		0.5		0.2
Ni			40			10		5		7
P	5	6	0.5	7	4	0.5	3	0.2	4	0.1
S	30	20	40	20	20	30	20	30	20	40
Si	40	50	10	100	40	20	200	10	100	7
Th			700			2,000		300		400
V			0.3			<0.2		<0.1		0.1
Ti			3			3		4		3

TABLE 3, Contd

Element	48 Surf			48 Core		
	H. T.	V/O	Aged	H. T.	V/O	Aged
Al	70	200	50	70	60	200
B			0.1			0.1
Ca	50	100	4	70	50	40
Cl			8			20
Co			1			2
Cr	500	1,000	50	1,000	1,000	100
Cu			2			10
Fe	~2,000	~7,000	200	~5,000	~7,000	400
K			0.3			1
Mg	2	3	3	2	2	7
Mn			20			60
Mo			4			20
Na			1			4
Ni	500	800	20	400	900	40
P	200	20	50	200	30	50
S	20	10	60	10	10	100
Si	300	100	50	200	100	400
Th			200			300
V			<0.2		<0.5	
Ti	<u><3</u>	<u><4</u>	10	<u><3</u>	<u><3</u>	20

TABLE 3, Contd

Element	49 Surf			49 Core			Efflusate From Vent of Capsule 49
	H. T.	V/O	Aged	H. T.	V/O	Aged	
Al	~3,000	200	~300	>3,000	900	~1,000	~2,000
B			0.1			0.1	<1
Ca	1,000	100	100	2,000	600	300	~4,000
Cl			10			10	50
Co			0.1			0.2	1
Cr	300	30	2	500	2,000	7	10
Cu			0.2			0.1	3
Fe	2,000	70	5	~3,000	~10,000	10	30
K			0.3			0.1	0.1
Mg	2	≤0.7	<0.3	3	4	2	<1
Mn			0.6			2	1
Mo			<0.5			1	6
Na			4			10	<1
Ni	400	7	0.6	500	2,000	0.7	2
P	~1,000	7	5	~1,000	40	20	4
S	10	10	20	30	20	30	9
Si	2,000	200	~500	3,000	1,000	~2,000	100
Th			300			200	15,000
V			<0.1			<0.03	<1
Ti	≤3	<0.5	1	≤3	5	2	900
Au							<10
Ba							10
Ce							4
Ir							~20,000
Ta							200
W							~8,000
Sr							10
Pu-239							major
Pu-238							major
Pu-240							20,000
Pu-241							5,000
Pu-242							400
U-234							4,000
Np-237							200

TABLE 4

Current Specifications for Impurities in GPHS Fuel
(DPST-79-1076)

<u>Element</u>	<u>Wt, ppm</u>
Al	150
B	1
Ca	300
Cd	50
Cr	250
Cu	100
Fe	800
Mg	50
Mn	50
Mo	250
Na	250
Ni	150
Pb	100
Si	200
Sn	50
Zr	50
Ti	No specification

Actinides

Am	} <1%
U	
Th	
Np	

No individual impurity is to exceed 1/2% by weight.

TABLE 5

Summary of PuO₂ Chemistry Comparing Results of Spark
Source Mass Spectroscopy (SSMS) and Emission Spectroscopy
(ES) for Major Impurities

Double entries for SSMS data refer to values for surface
and core samples. Values are weight ppm.

Element	Pellet 44			Pellet 45		
	SSMS	Aged	ES	SSMS	Aged	ES
	V/O		Aged	HT		Aged
Al	30/30	5/10	60	50/60	3/10	60
Ca	2/2	6/10	15	4/3	0.3/7.0	15
Cr		70/20	<5		20/10	6
Fe	1000/900	300/100	30	800/2000	100/70	20
Mg		1	<1		7/5	<1
Ni		40/10	<5		0.5/0.2	<5
P	6/4	0.5/0.5	5*	3/4	0.2/0.1	5*
S	20/20	40/30	-	20/20	30/40	-
Si	50/40	10/20	35	200/100	10/7	30
Ti		3/3	10		4/3	7

Element	Pellet 48			Pellet 49		
	SSMS	Aged	ES	SSMS	Aged	ES
	V/O		Aged	V/O		Aged
Al	200/60	50/200	65	200/900	300/1000	190
Ca	100/5	40/40	15	100/600	100/300	200
Cr	1000/1000	50/100	9	30/2000	2/7	<5
Fe	7000/5000	200/400	25	70/10,000	5/10	7
Mg	3/2	3/7	<1	<7/4	<3/2	<1
Ni	800/900	20/40	<5	7/2000	0.6/0.7	<5
P	20/30	50/50	20*	7/40	5/20	35*
S	10/10	60/100	-	10/20	20/30	-
Si	100/100	50/400	50	200/1000	500/2000	170
Ti	<4/<3	10/20	10	<0.5/5	1/2	8

* Determined by colorimetry at LANL

FIGURE X.6 Orientation of Compatibility Test Pellets in Aging Furnace.

- Large quantities of Al, Ca, and Si added to Pellet 49 formed a second phase in the grain boundaries during fabrication. During aging these elements were redistributed to the pores and free surfaces such as internal cracks (Figure 7). Transport out of the fuel, most likely by vaporization, followed a pathway of migration from the interior of the fuel to free surfaces (e.g. cracks). A small amount of second phase deposit was also seen in Pellet HF-2 (from ECT-1). Impurities in Pellet HF-2 were Si, 170 ppm; Al, 268 ppm; Ca, 75 ppm. Current specifications for each of these impurities are Si, 200 ppm; Al, 150 ppm; and Ca, 100 ppm. The presence of an identifiable second phase in pellets HF-2 and 49 suggests that the specification limits for Si, Al and Ca ought to be set lower than about 100 ppm since no second phase has been observed in pellets for which these three impurities were less than about 100 ppm (which is normally the case for production pellets).
- Fe and Cr impurities present in the pre-aged fuel at different levels were reduced during aging but not to a common or "equilibrium" value.
- Although the composition of Pellet 48 was intended to differ from Pellet 44 and 45 only in P, evidence from examination of the vents and cladding suggests that the composition of Pellet 48 was significantly higher in elements such as Si. Bulk analyses by SSMS and emission spectroscopy (ES) were conflicting and could not resolve this issue.

Fuel Structure

- Generally, aging tended to slightly densify the fuel. Grain size increased by up to a factor of approximately two.
- Aging does not significantly multiply the number of cracks in the fuel.

Effect of Aging on Iridium Cladding

Iridium Microstructure

- The grain size of the fueled cups is greater in all cases than that of the aged archive rings or unfueled aged cups (Table 6, Figures 8 through 12).
- The interior grains of the fueled iridium cups (those nearest the fuel) are larger on average than the grains at the center of the thickness of the cups or at the exterior of the cups (Table 6).

TABLE 6

Average Grain Size of Iridium

Comparison of Pre-Aged, Aged but Unfueled, and Aged and Fueled Iridium

Grain size measured axially 100 μm from surface next to fuel (interior), a long center line of iridium thickness (center), and 100 μm from surface next to graphite (exterior). Measurements made on several photomicrographs to improve statistics.

Grain size given in micrometers, μm

Location	Pellet Number	Archive Rings (Unfueled Control Samples)				Cups (Fueled Iridium)		(Unfueled)	
		Pre-Aged		Aged		Aged		Aged	
		Vent*	Shield**	Vent	Shield	Vent	Shield	A	B
Exterior	44	46	46	72	66	110	100		
	45	42	55	56	71	87	111		
	48	58	39	82	53	301	107		
	49	<u>79</u>	<u>54</u>	<u>90</u>	<u>78</u>	<u>126</u>	<u>115</u>		
	Average	56	49	75	67	156	108	72	64
Center	44	38	51	68	65	72	66		
	45	37	44	50	66	82	101		
	48	51	37	74	57	91	88		
	49	<u>54</u>	<u>41</u>	<u>79</u>	<u>74</u>	<u>90</u>	<u>104</u>		
	Average	45	43	68	66	84	90	63	65
Interior	44	43	47	56	57	167	197		
	45	50	58	50	89	182	138		
	48	54	68	72	64	188	128		
	49	<u>77</u>	<u>39</u>	<u>73</u>	<u>53</u>	<u>217</u>	<u>131</u>		
	Average	56	53	63	66	189	149	82	71
Overall Average		52	48	69	66	143	116	72	67

* Refers to archive ring from vent cup (cup having vent hole) used to encapsulate given pellet.

** Refers to archive ring from shield cup (cup having welding shield) used to encapsulate given pellet.

1-21-

SEM
Image

Al

Ca

Si

Pu

O

Ti

P

Second Phase
No Longer at
Grain Boundaries
or in Pores

Second Phase in Pores

Second Phase

FIGURE 7. Pellet 49: (a) Second Phase (light gray) on Internal Crack Surface and in Pores Near the Crack Surface; (b) Microprobe Electron Dot Maps Showing Composition of Second Phase. The given element appears bright in the dot maps.

X-ray

FIGURE 8. Capsule 44, Comparison of Unaged and Aged Archive Rings to Aged Fueled Iridium Clads: (a) Vent Cup (L 256-8); (b) Shield Cup (L 254-7). The bottom of each micrograph is the concave or interior surface (surface next to fuel for cups).

FIGURE 45. Capsule 45, Comparison of Unaged and Aged Archive Rings to Aged Fueled-Iridium Clads: (a) Vent Cup (L 257-R2); (b) Shield Cup (L 255-6). The bottom of each micrograph is the concave or interior surface (surface next to fuel for cups).

FIGURE 10. Capsule 48, Comparison of Unaged and Aged Archive Rings to Aged Fueled Iridium Clads: (a) Vent Cup (P 701-4); (b) Shield Cup (N 502-3). The bottom of each micrograph is the concave or interior surface (surface next to fuel for cups).

FIGURE 10
Continued Capsule 48, Vent Cup Showing Areas of Large Grains at
Both the Exterior Edge (top of micrographs) and Interior
Edge (bottom of micrographs).

Unaged Archive Rings

Aged Archive Rings

Aged Cups

FIGURE 6. Capsule 49, Comparison of Unaged and Aged Archive Rings to Aged Fueled Iridium Clads: (a) Vent Cup (P 714-5); (b) Shield Cup (PR 715-2). The bottom of each micrograph is the concave or interior surface (surface next to fuel for cups).

Unaged Archive Rings

Aged Archive Rings

Aged Cups

FIGURE ¹² ~~1~~. Capsule T-40 (Unfueled Control), Comparison of Unaged and Aged Archive Rings to Aged Iridium Clads: (a) Top Cup (NR 520-2); (b) Bottom Cup (PR 719-6). The bottom of each micrograph is the concave or interior surface.

- The interior and exterior grains of the unfueled aged cups are also slightly larger than the center grains of their cups (Table 6).
- The grain size of the aged archive rings is essentially uniform across the thickness (Table 6, Figures 8 through 12).
- The vent cup of Pellet 48 (P-701-4) had areas of widely varying grain size with very large grains on both interior and exterior surfaces. The shield cup on Pellet 49 (PR-715-2) also showed areas of variable grain size (variable refers to fluctuations in grain size in the direction parallel to the longitudinal axis of the cups and at the same depth) with areas of unusually large grains on the exterior surface (Table 6, Figure 10).
- The effect on iridium microstructure of the different pellets was only evident as a larger average grain size for the vent cups of Pellets 48 and 49 (Table 7).

Iridium Chemistry

- Phosphorus (P) was detected by Auger electron spectroscopy (AES) in the cladding of Pellets 48 and 49 corresponding to the levels in the fuel. The AES analysis for this and all samples was taken using an electron beam with a 15 μm beam diameter. Spectra were obtained from three locations on each Ir sample: about 100 μm from both the inside and outside edges and one in the center of the cross section. For CVS 48 with 20 ppm P in the fuel, P was not detected uniformly on the Ir grain boundaries. Instead it appeared in patches and was found only at the center and exterior surface of the cups. With CVS 49 which had 35 ppm P in the fuel, P was detected throughout the Ir grain boundaries. In contrast, P was not detected in the iridium cladding of Pellets 44 and 45. P in both of these pellets was less than 10 ppm. Based on this result we are recommending a maximum P level in the fuel of less than or equal to 15 ppm. The effect on P transport by other impurities could not be determined in this study.
- For Capsules 48 and 49, P was detected at Ir grain boundaries by AES, but its presence could not be correlated with grain growth. For example, the shield cup of Capsule 48 (N-502-3) had uniform Th content and grain size across the thickness at the location examined by AES (different from that shown in Figure 10. P was detected at grain boundaries of center and exterior grains and not on the interior grain boundaries. No large grains associated with the location of the P were observed.

TABLE 7

Comparison of Grain Size of Iridium Cups from Each Fuel Pellet, μm

Thorium content (expressed as $\text{Th}_{65}/\text{Ir}_{229}$ Auger peak height ratio) are included for reference.

Location	Vent Cups							
	Pellet 44		Pellet 45		Pellet 48		Pellet 49	
	Grain	Th_{65}	Grain	Th_{65}	Grain	Th_{65}	Grain	Th_{65}
Cross Section	Size	Ir_{229}	Size	Ir_{229}	Size	Ir_{229}	Size	Ir_{229}
Exterior	110	0.43	87	0.57	301	0.40	126	0.46
Center	72	0.59	82	0.65	91	0.43	90	0.64
Interior	<u>167</u>	<u>0.33</u>	<u>182</u>	<u>0.24</u>	<u>188</u>	<u>0.0</u>	<u>217</u>	<u>0.21</u>
Average	116	0.45	117	0.49	193	0.28	144	0.44
	Shield Cups							
	Grain	Th_{65}	Grain	Th_{65}	Grain	Th_{65}	Grain	Th_{65}
	Size	Ir_{229}	Size	Ir_{229}	Size	Ir_{229}	Size	Ir_{229}
Exterior	100	0.46	111	0.27	107	0.68	115	0.77
Center	66	0.74	101	0.69	88	0.49	104	0.61
Interior	<u>197</u>	<u>0.41</u>	<u>138</u>	<u>0.31</u>	<u>128</u>	<u>0.61</u>	<u>131</u>	<u>0.56</u>
Average	121	0.54	117	0.42	108	0.59	117	0.65
Average of Both Cups	119	0.50	117	0.46	151	0.44	131	0.51

Average Th for all cups = 0.48 ± 0.11 .

- Th was investigated by SSMS, AES, and secondary ion mass spectrometry (SIMS). No significant change in bulk concentration was found by SSMS (Table 8). AES results suggested a general Th depletion on the grain boundaries of all fueled aged cups compared to aged archive rings (Table 9). The interior grains showed the most depletion, the center grains the least and the exterior grains depletion intermediate between that of the center and interior grains (Table 9). A plot of Th content for each region (exterior, center, interior) averaged over all cups versus grain size for each region averaged over all cups showed a fairly linear correlation, with the grain size increasing as the Th content decreased (Table 10, Figure 13). Comparing the CVS for each capsule, the average Th content of each CVS did not significantly differ one from another (Table 7). However, with respect to individual cups, the Th content of the vent cup of Capsule 48 is greater than one standard deviation lower than the average Th content of all cups and the Th content of the shield cup of Capsule 49 is greater than one standard deviation higher than the average of all cups. Hence, the effect of impurities on the Th content of the iridium cladding is inconclusive. The SIMS data showed Th on the grain boundaries. The number of Th inclusions appeared to be fewer than for unaged iridium.

- The Ir was analyzed for several other elements using SIMS, SSMS, and ES. The SSMS samples were run with standards and were accurate to within about +30%. The results for key elements follow (also see Table 8).
 - Tungsten (W). No change in W concentration was reported by SIMS. The results of the SSMS analyses were unclear. In all cases but one (Pellet 45), the W level was reported to have increased by a factor of 2 to 3. Since the precision of the measurements is about +30%, the measured increase is apparently real. However, since there is no known source of W at present the measured increase in W is not understood. W is added to the Ir to increase the recrystallization temperature and thereby inhibit grain growth. Normally W is homogeneously distributed throughout the Ir.

 - Silicon (Si) was found along the grain boundaries in the Ir by SIMS at only low levels. No metallographic evidence for any second phase was found except near the vent holes. Hence, fracture along the longitudinal side of the CVS's due to a brittle Ir/Si intermetallic is unlikely. SSMS showed a slight increase in bulk Si content from less than or equal to 1 ppm to approximately 7 ppm. The weld in Sample 45 was measured at 20 ppm. Samples of weld areas were not available for examination by SIMS for Si along grain boundaries.

TABLE 8

Iridium Chemistry

Comparison of unaged and aged archive rings to aged fueled cups by Spark Source Mass Spectroscopy (SSMS), ppm. Analyses of selected aged fueled cups by Emission Spectroscopy (ES) is also included. Dash (-) indicates no data.

Element	Pellet 44: Vent Cup			Cup by ES	Pellet 44: Shield Cup			Cup by ES	Pellet 44 Weld
	Archive Ring		Cup		Archive Ring		Cup		
	Unaged L-256-8	Aged			Unaged L-254-7	Aged			
Al	27	24	53		15	29	60		38
B	0.1	<0.01	<0.01		0.01	<0.01	<0.01		<0.01
Ca	1	1	2		0.4	0.7	0.7		0.8
Co	-	<0.03	0.3		-	<0.05	0.2		<0.05
Cr	0.7	0.4	0.5		0.3	2	5		1
Cu	7	1	2		3	2	2		1
Cl	-	0.5	0.05		-	0.1	0.2		0.2
Fe	6	7	10		10	20	30		20
Ir	M	M	M		M	M	M		M
K	-	0.5	0.1		-	0.1	0.2		0.1
Mg	-	<0.05	<0.3		-	0.1	<0.09		<0.03
Mn	-	0.03	0.1		-	3	0.2		0.07
Mo	<0.5	7	1		1	0.5	1		1
Na	0.1	0.4	0.3		0.05	0.07	0.3		0.3
Ni	<0.5	<0.2	0.8		2	0.5	3		4
P	0.02	0.04	0.1		0.03	<0.03	0.1		0.03
Pt	<1	<2	<3		<5	20	<3		<2
Re	-	<1	<1		-	20	10		10
Rh	0.6	0.6	0.7		0.8	0.5	0.7		0.7
Ru	7	5	8		3	7	6		7
S	2	3	7		2	3	7		4
Si	1	2	5		1	1	7		2
Ta	<20*	-	-		<40*	-	-		-
Th	50	39	57		36	45	48		36
Ti	<0.2	-	-		<0.3	-	-		-
V	-	<0.1	0.3		-	0.1	0.2		<0.1
W	2800	3800	5900		2500	2000	7700		3200
Zr	0.1	-	-		0.2	-	-		-

* Source made from Ta.

TABLE 8, Contd

Element	Pellet 45: Vent Cup			Cup by ES	Pellet 45: Shield Cup			Cup by ES	Pellet 45 Weld
	Archive Ring		Cup		Archive Ring		Cup		
	Unaged	Aged			Unaged	Aged			
	L-257-R2				L-255-6				
Al	43	45	48		10	36	150	170	
B	0.02	0.01	<0.01		0.02	<0.01	<10	<0.01	
Ca	1	0.7	0.7		0.5	0.7	<3	1	
Co	-	<0.03	<0.3		-	<0.03	<10	0.2	
Cr	3	0.4	3		0.5	0.3	20	8	
Cu	40	2	2		2	1	10	5	
Cl	-	0.05	0.2		-	0.1	-	0.1	
Fe	20	3	5		2	2	300	40	
Ir	M	M	M		M	M	M	M	
K	-	0.1	0.3		-	0.1	<3000	0.3	
Mg	-	<0.05	<0.03		-	<0.02	3	<0.1	
Mn	-	0.1	<0.05		-	<0.05	<30	0.3	
Mo	<0.5	1	0.7		1	0.7	<200	0.7	
Na	0.05	0.07	1.4		0.1	0.1	<300	1	
Ni	1	0.2	1		<0.3	0.3	40	3	
P	0.03	<0.01	0.1		0.02	<0.02	<300	0.2	
Pt	<5	<4	<2		<5	<2	<30	<2	
Re	-	<1	5		-	4	-	7	
Rh	0.5	0.5	0.5		1	0.7	<30	1	
Ru	5	4	4		10	7	<30	7	
S	6	4	3		2	3	-	5	
Si	2	1	6		5	<1	<10	20	
Ta	<50*	-	-		<10*	-	<1000	-	
Th	60	70	40		20	75	-	52	
Ti	<0.2	-	-		<0.1	-	<30	-	
V	-	0.3	<0.1		-	<0.1	<30	<0.2	
W	3100	3800	2700		2900	2900	1000- 10,000	3600	
Zr	0.2	-	-		0.1	-	<200	-	

* Source made from Ta.

TABLE 8, Contd

Element	Pellet 48: Vent Cup			Cup by ES	Pellet 48: Shield Cup			Cup by ES	Pellet 4 Weld
	Archive Ring		Cup		Archive Ring				
	Unaged	Aged			Unaged	Aged	Cup		
	P-701-4				N-502-3				
Al	26	28	49	70	34	21	50	47	
B	<0.02	<0.01	<0.01	<10	0.02	<0.01	<10	<0.01	
Ca	1	0.4	1	<3	0.5	0.7	3	1	
Co	-	<0.03	<0.05	-	-	<0.03	<10	<0.05	
Cr	1	0.2	2	<10	0.7	0.5	<10	-	
Cu	3	1	1	5	3	3	15	3	
Cl	-	0.05	0.1	-	-	0.07	-	<0.05	
Fe	2	1	10	150	3	3	170	10	
Ir	M	M	M	-	M	M	M	M	
K	-	0.1	0.07	<3000	-	0.08	<3000	0.1	
Mg	-	<0.04	<0.02	<3	-	<0.01	<3	<0.02	
Mn	-	0.05	0.2	<10	-	0.07	<10	<0.1	
Mo	0.3	0.5	0.7	<200	<0.5	3	<200	1	
Na	0.4	0.1	0.2	<300	0.05	0.05	<300	0.2	
Ni	1	0.1	2	10	0.3	0.4	20	0.7	
P	0.05	<0.02	0.06	<300	0.02	<0.01	<300	0.04	
Pt	<7	<2	<3	<30	<1	<1	<30	<2	
Re	-	<1	<2	-	-	<1	-	<1	
Rh	<0.05	0.4	0.7	<30	1	0.5	<30	<0.5	
Ru	<0.3	1	1	<30	10	3	<30	6	
S	6	1	3	-	2	2	-	3	
Si	<2	<1	7	10	<1	<1	5	7	
Ta	<5*	-	-	<1000	<20*	-	<1000	-	
Th	27	43	36	-	53	35	-	41	
Ti	<0.2	-	-	<30	<10	-	<30	-	
V	-	<0.1	<0.3	<30	-	<0.06	<30	0.3	
W	2800	2600	3900	1000-	3100	2900	1000-	2900	
				10,000	-		10,000		
Zr	0.2	-	-	<200	0.1	-	<200	-	

* Source made from Ta.

TABLE 8, Contd

Element	Pellet 49: Vent Cup			Cup by ES	Pellet 49: Shield Cup			Cup by ES	Pellet 4 Weld
	Archive Ring		Cup		Archive Ring		Cup		
	Unaged	Aged			Unaged	Aged			
	P-714-5				PR-715-2				
Al	27	46	56	80	48	15	75	60	45
B	0.01	<0.01	<0.01	<10	0.01	<0.01	<0.01	<10	<0.01
Ca	0.3	0.7	2	<3	0.7	0.5	3	3	1
Co	-	<0.06	<0.04	-	-	<0.03	0.2	-	<0.07
Cr	0.8	5	1	40	0.3	0.5	3	40	2
Cu	2	4	3	10	5	2	4	15	3
Cl	-	0.3	0.3	-	-	0.2	0.2	170	0.07
Fe	7	20	10	300	2	5	20	-	10
Ir	M	M	M	-	M	M	M	M	M
K	-	0.1	0.1	<3000	-	0.07	0.3	<3000	0.1
Mg	-	<0.1	<0.04	<3	-	<0.05	<0.03	<3	<0.05
Mn	-	0.3	0.5	<10	-	0.08	0.2	<10	0.2
Mo	<0.5	0.5	0.7	<200	<0.1	1	0.7	<200	<0.5
Na	0.1	0.1	0.3	<300	0.07	0.07	0.5	<300	2.4
Ni	0.7	0.5	0.7	40	0.1	0.3	1	30	0.7
P	0.03	0.04	0.07	<300	0.01	<0.03	0.7	<300	0.1
Pt	<7	<2	<2	<30	<2	<3	<2	<30	<2
Re	-	<1	<1	-	-	<1	<1	-	<1
Rh	2	0.1	<0.01	<30	<0.05	0.4	<0.3	<30	<0.2
Ru	<0.5	<0.5	0.7	<30	<0.4	5	2	<30	1
S	2	5	5	-	3	3	5	-	4
Si	2	1	8	10	<0.7	<0.05	7	7	7
Ta	<20*	-	-	<1000	<10*	-	-	<1000	-
Th	46	55	52	-	65	34	55	-	59
Ti	<0.2	-	-	<30	<0.1	-	-	<30	-
V	-	<0.05	<0.1	<30	-	<0.07	0.2	<30	<0.07
W	3200	1900	2700	1000-	3600	2400	3600	1000-	3900
				10,000				10,000	
Zr	0.3	-	-	<200	0.1	-	-	<200	-

* Source made from Ta.

TABLE 8, Contd

Element	Unfueled Capsule, T-40			Cup by ES	Unfueled Capsule, T-40			Cup by ES	T-40 Weld
	A, Top Cup				B, Bottom Cup				
	Archive Ring				Archive Ring				
	Unaged	Aged	Cup		Unaged	Aged	Cup		
	NR-520-2				PR-719-6				
Al	13	25	44		49	26	35		34
B	<0.01	<0.01	<0.01		0.04	<0.01	<0.01		<0.01
Ca	1	0.5	1		5	0.7	0.8		1
Co	-	<0.04	0.03		-	<0.02	<0.04		<0.1
Cr	1	0.4	0.5		2	0.3	<0.5		2
Cu	10	3	4		20	3	3		4
Cl	-	0.1	0.2		-	0.07	0.3		0.7
Fe	10	3	2		10	1	4		7
Ir	M	M	M		M	M	M		M
K	-	0.2	0.08		-	0.1	0.1		0.3
Mg	-	<0.07	<0.05		-	<0.02	<0.05		<0.1
Mn	-	0.04	<0.02		-	0.05	<0.05		<0.05
Mo	<1	1	1		10	0.5	2		4
Na	0.1	0.1	0.2		1	0.07	0.2		0.3
Ni	0.7	0.4	0.5		4	0.3	0.7		2
P	0.03	<0.03	0.4		0.05	<0.02	0.05		0.1
Pt	<2	2	<0.5		<10	<1	<2		<2
Re	-	<1	<1		-	<1	<1		<1
Rh	2	1	1		3	0.8	0.4		1
Ru	10	10	10		10	4	3		10
S	4	3	3		10	3	4		5
Si	2	2	3		10	1	3		3
Ta	<20*	-	-		<20*	-	-		-
Th	46	57	60		42	55	34		36
Ti	<0.4	-	-		<0.5	-	-		-
V		<0.1	0.2		-	<0.05	<0.05		<0.05
W	2500	2400	2300		3500	2600	3400		2500
Zr	0.1	-	-		3	-	-		-

* Source made from Ta.

TABLE 9

Thorium Content of Iridium Grain Boundaries

Comparison of Pre-Aged, Aged but Unfueled, and Aged and Fueled Iridium. Thorium content measured by Auger electron spectroscopy (AES) at LANL and expressed as $\text{Th}_{65}/\text{Ir}_{229}$ peak height ratio. Electron beam spot size about 15 μm . Three readings were taken across the iridium cross-section; one at about 100 μm from each edge and one at the center.

Location	Pellet Number	Archive Rings (Unfueled Control Samples)				Cups (Fueled Iridium)	
		Pre-Aged		Aged		Aged	
		Vent*	Shield**	Vent	Shield	Vent	Shield
Exterior	44	0.80	0.70	0.74	0.88	0.43	0.46
	45	0.55	0.87	0.90	0.66	0.57	0.27
	48	0.75	0.64	0.64	0.82	0.40	0.68
	49	0.73	0.66	0.87	0.81	0.46	0.77
	T-40†	0.71	0.65	0.70	0.84	(0.77††)	(0.67††)
	Average	0.71	0.70	0.77	0.80	0.47	0.55
		$\sigma = 0.09$	$\sigma = 0.10$	$\sigma = 0.11$	$\sigma = 0.08$	$\sigma = 0.07$	$\sigma = 0.22$
Center	44	0.66	0.88	0.87	0.97	0.59	0.74
	45	1.08	0.96	0.88	1.03	0.65	0.69
	48	0.84	0.91	0.86	0.61	0.43	0.49
	49	0.68	0.84	0.71	1.01	0.64	0.61
	T-40†	0.78	0.94	0.85	1.13	(0.88††)	(0.74††)
	Average	0.81	0.91	0.83	0.95	0.58	0.63
		$\sigma = 0.17$	$\sigma = 0.05$	$\sigma = 0.07$	$\sigma = 0.20$	$\sigma = 0.10$	$\sigma = 0.11$
Interior	44	0.80	0.78	0.66	0.44	0.33	0.41
	45	0.82	0.80	0.94	0.71	0.24	0.31
	48	0.57	0.60	0.69	0.84	-	0.61
	49	0.61	0.74	0.72	0.85	0.21	0.56
	T-40†	0.89	0.91	0.75	0.97	(0.73††)	(0.75††)
	Average	0.74	0.77	0.75	0.76	0.20	0.47
		$\sigma = 0.14$	$\sigma = 0.11$	$\sigma = 0.11$	$\sigma = 0.20$	$\sigma = 0.14$	$\sigma = 0.14$
Overall Average		0.75	0.79	0.79	0.84	0.41	0.55
		$\sigma = 0.13$	$\sigma = 0.12$	$\sigma = 0.10$	$\sigma = 0.18$	$\sigma = 0.19$	$\sigma = 0.16$

* Refers to archive ring from vent cup used to encapsulate given pellet.

** Refers to archive ring from shield cup used to encapsulate given pellet.

† T-40 refers to unfueled capsule consisting of two shield cups welded together and aged in graphite as a further control sample

†† Values in parentheses not included in column average.

TABLE 10

Comparison of Grain Size Versus Thorium Content for Aged Iridium Cups

Location	Pellet Number	Vent Cups		Shield Cup		Capsule Average	
		Grain Size, μm	Thorium Content, Th ₆₅	Grain Size, μm	Thorium Content, Th ₆₅	Grain Size, μm	Thorium Content, Th ₆₅
			Ir ₂₂₉		Ir ₂₂₉		Ir ₂₂₉
Exterior	44	110	0.43	100	0.46	105	0.45
	45	87	0.57	111	0.27	99	0.42
	48	301	0.40	107	0.68	204	0.54
	49	<u>126</u>	<u>0.46</u>	<u>115</u>	<u>0.77</u>	<u>121</u>	<u>0.62</u>
	Average	156	0.47	108	0.55	132	0.51
	(T-40*)	(72)	(0.77)	(64)	(0.67)	(68)	(0.72)
Center	44	72	0.59	66	0.74	69	0.66
	45	82	0.65	101	0.69	91	0.67
	48	91	0.43	88	0.49	90	0.46
	49	<u>90</u>	<u>0.64</u>	<u>104</u>	<u>0.61</u>	<u>97</u>	<u>0.63</u>
	Average	84	0.58	90	0.63	87	0.61
	(T-40)	(63)	(0.88)	(65)	(0.74)	(64)	(0.81)
Interior	44	167	0.33	197	0.41	182	0.37
	45	182	0.24	138	0.31	160	0.28
	48	188	-	128	0.61	158	0.31
	49	<u>217</u>	<u>0.21</u>	<u>131</u>	<u>0.56</u>	<u>174</u>	<u>0.39</u>
	Average	189	0.20	149	0.47	169	0.34
	(T-40)	(82)	(0.73)	(71)	(0.75)	(77)	(0.74)
Overall Average		143	0.42	116	0.55		

* T-40 = unfueled capsule.

FIGURE 8. Average Thorium Content by AES Vs. Average Grain Size.

- Iron (Fe) and Chromium (Cr) were detected in large amount by SIMS in the Ir. Nickel (Ni) was also detected, but in smaller quantities. For Capsule 49 the concentration was maximum at the interior surface (approximately 1/2 atom % for Fe) and decreased to background at a depth of about 150 μm . For Capsule 44, the maximum concentration of Fe and Cr was approximately the same as that of Capsule 49 at the surface but the depth of penetration was only about 30 μm . The concentration of Fe and Cr at the surface of Capsule 45 was also approximately the same as for Capsule 49. The depth of penetration was about midway between Capsules 44 and 49. SIMS showed that the concentration of Fe and Cr was maximum at the iridium grain boundaries and fell off with depth into the grains from the grain boundaries. Near the surface of the iridium the concentration fell off very little from the maximum at the grain boundary. However, the fall off became sharper with depth into the iridium until at the maximum depth of penetration, the Fe and Cr were located only at the grain boundaries. Fe was also shown to diffuse more rapidly along the grain boundaries and into the bulk iridium. The SIMS data graphically demonstrate that the Fe and Cr diffuse rapidly into the Ir along grain boundaries and from the grain boundaries into the bulk iridium. Fe and Cr were not detected at the grain boundaries by AES. However, the AES spectra were taken at about 100 μm in from the edge of the iridium where the Fe and Cr concentration had fallen off sharply and was probably below the detection limits of the Auger spectrometer. Previous work at ORNL⁵ could detect no effect of Fe on grain size for concentrations of Fe in the Ir up to 300 ppm. Higher concentrations were not evaluated, but no effects on grain size of Fe and Cr could be positively identified in the present study. The boundary of the Fe and Cr diffusion layer was not as deep as the boundary of the large grain size. In addition the Fe and Cr diffusion boundaries for Ir clads of Capsules 44 and 45 were at different depths whereas the boundaries of the large grains were about the same as for Capsule 49. Hence, Fe and Cr probably do not have a strong effect on grain growth.
- Calcium (Ca) was not observed at the grain boundaries by SIMS. No change in the Ca level was observed by SSMS for any sample except Capsule 49. There the Ca increased six-fold from 0.5 ppm to 3.0 ppm.
- Aluminum (Al) was found by SIMS to correlate with the presence of Fe and Cr, decreasing as the inverse of the increase in the Fe and Cr concentration. In particular the concentration of Al at grain boundaries was specifically lowered where Fe and Cr were present. The bulk concentration measured by SSMS was erratic. Some samples showed an increase by nearly a factor of two, while others showed no increase. At concentrations

up to about 100 ppm ORNL⁵ found that Al appeared to improve impact ductility. From the SIMS and SSMS results of the present work the effect on impact ductility of the changes in Al concentration and distribution appear indeterminate. If the effect of the Al results from its presence on grain boundaries, then the ductility is probably impaired by the Fe and Cr. If the effect of the Al depends on its bulk concentration, then the Fe and Cr probably have relatively little effect since the bulk Al concentration did not seem affected except near the inner edge.

Effect of Aging on Vents

Vent Chemistry

- In general, impurities volatilizing from the fuel deposit on interior surfaces of capsules as well as in vents. The extent of this deposition varies from sample to sample and with location within the sample.
- No deposits around the vent holes on the exterior of the clads were observed for Capsule 45 (not outgassed, Figure 14). Minor surface desposits were found on Capsule 44 (Figure 15). Very extensive deposits of impurites (approximately 6.3 mg) were found forming a cone around the vent of Capsule 49 (Figure 16). Deposits around Capsule 48 vent hole (Figure 17) were heavier than for Capsule 44, but these may have come from Capsule 49 by vapor migration through the holes in the graphite floating membrane separating Capsule 48 from Capsule 49. Evidence for this can be seen by the hexagonal pattern of spots visible on the Ir of Capsule 48 which correspond to the holes in the graphite membrane.
- Capsule 45 had the least deposits in the filter elements. Capsules 44, 48, and 49 all had large amounts of material deposited in the filter elements (Figure 18). Considering all the photomicrographs of the filter elements (not just those shown in Figure 18) Capsule 49 was judged to have more material in the filter elements than Capsules 44 and 48.
- Deposits of about the same composition as those observed in the vent filter elements were also observed around the vent holes.
- Microprobe analysis of the deposits in the vents (filter element and vent hole) showed these deposits consisted of a major phase and one or more minor phases. The major phase consisted of the dopant elements (Ca, Al, Si, P, and Pu) in various amounts as well as some unexpected elements present in the fuel at low levels (e.g. Mg, Ti).

a

b

FIGURE 14 (a) Surface of Capsule 45 Showing Lack of Deposits Around Vent Hole; (b) Inner Surface of Cups.

a

b

FIGURE 15. (a) Surface Deposits Around Vent Hole in Capsule 44;
(b) Deposits on Inner Surface of Shield Cup.

Effusate

a

c

b

d

FIGURE 16

(a) Effusate Rising Above Vent Hole in Capsule 49;
(b) End-on View of Vent Hole and Effusate; (c) Inner
Surface of Cups; (d) Typical Configuration of PuO_2
Fuel in Capsules.

a

b

FIGURE 12. (a) Surface Deposits Around Vent Hole in Capsule 48;
(b) Deposits on Inner Surface of Cups.

a

b

c

d

e

FIGURE 13. Impurity Deposits in Filter Elements (a) Configuration of a Typical GPHS Vent; (b) Vent, Capsule 45; (c) Vent, Capsule 44; (d) Vent, Capsule 48; (e) Vent, Capsule 49.

- The major phase was found throughout the filter elements.
- The qualitative composition of the phases found in each capsule vent are given in Table 11.
- For undoped fuel samples, the major impurity phase in the filter elements consisted of Ca, Si, Mg, and Pu (similar to that for Capsule 48, Figure 19, except richer in Si and Mg, and having no P).
- The material in the vents of Capsule 48 reflect the P in the fuel. Microprobe data suggest the phase formed in the undoped sample vents was modified in Capsule 48 by P replacing Si (Figure 19). This substitution is common for compounds with phosphates and silicates.
- The effect of the high concentrations of Si and Al are apparent in the major phase in the vent of Capsule 49. Even though P is present, the extra Si in the fuel evidently led to an increase in Si in the deposit (Figure 20). The excess Al replaced the Mg. This phase was decorated with dendrites of Ca-Pu which appear to have recrystallized from the compound suggesting the compound may have been liquid at the aging temperature.
- Near the center of the vents, deposits of nearly pure SiO_2 are found reflecting the high volatility of the Si-O species.
- At the surface near the vent hole intermetallic compounds of Ir, Si, and Pu begin to form (Figure 21).
- In Capsule 48 an Ir-W intermetallic is observed in the vent hole (Figure 22).
- In Capsule 49 Ir-Ti and Ir-Al intermetallics begin to form.
- Deposits of Ca, Al, and Si are found in the grain boundaries near the vent hole in Capsule 49 (Figure 23).
- The numerous minor phases show the complexity of the volatile species. It is significant that they contain no other elements than those contained in the major phases.
- The results show that the additions of large amounts of Ca, Al, and Si increase the volatilization of Pu. Pu analysis of the graphite surrounding Capsules 48 and 49 show the Pu transport out of the capsules to be approximately ten times greater than for undoped Pellets 44 and 45 (445 μg vs. 61 μg). However, the recovery of the effusate surrounding the vent hole of Capsule 49 (6.3 mg) shows the amount of Pu volatilized is probably several orders of magnitude greater than for undoped samples.

TABLE 11

Qualitative Composition of Phases Identified in Vents

(Elements listed in apparent order of abundance)

<u>Phase</u>	<u>Capsule</u>	<u>Elemental Composition</u>
1	44, 45	Ca, Si, Mg, Pu, Al (contains Ca-Pu dendrites)
2	44, 45	Pu, O
3	44	Ca, Pu, O
4	44	Si, Mg, Ir
5	48	Ca, Pu, Mg, P, Si, O
6	48	Si, Mg, Ca, Pu
7	48	Ti, Al
8	49	Si, Ca, Al, Pu, O, P, Ti
9	49	Ca, P
10	44, 48, 49	Si, O
11	45, 48	Al, Ca, O, Pu
12	45	Ca, Al, O, Si, Pu
13	45	Ta, Ca, O, Al, Pu, Th, U, Si
14	49	Si, O, Pu, Ca, Al, Ti
15	44	Ca, Al, Pu, Si, O, Ti
16	44	Ca, Pu, Si, O
17	48	Ir, Si, Pu
18	48	Ir, Si, Pu, O
19	48	Pu, O, Al, Ca, Si
20	48	Cr, O, Fe, Mg, Al
21	49	Ir, Ti
22	49	Ir, Al

FIGURE 14. ¹⁹ ~~14~~ ^{X-ray} Microprobe Electron Dot Images of Impurity Deposits in Filter Element of Capsule 48.

SEM

Ir

Si

Al

Ca

Pu

P

O

FIGURE 15. ⁷⁰ ^{X-ray} Microprobe Electron Dot Images of Impurity Deposits in Filter Element of Capsule 49.

Ir

Pu

Si

O

FIGURE 16. ²¹ Microprobe ^{X-ray} Electron Dot Images of Ir - Si - Pu Intermetallic Formed at Outside Surface of Capsule 48 Near Vent Hole.

FIGURE 17. Ir - W Intermetallic and Oxide Deposits in Vent Hole in Capsule 48.

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FIGURE 18. Deposits of Ca, Al, and Si in Iridium Grain Boundaries Near Vent Hole of Capsule 49: (a) Impurities Decorating Grain Boundaries in As-Polished Iridium; (b) Etched to Reveal Grain Boundaries; (c)-(d) Microprobe Electron Dot Images of Grain Boundary Deposits in Region Shown in (a).

Effect of Vacuum Outgassing

The vent in Capsule 45 was noticeably more free of deposits than the vents of the other three capsules. It is unlikely that this result is due to a significantly lower level of impurities in Pellet 45. For example, chemical analyses of Pellets 44 and 45 by both SSMS and ES found no significant difference in their composition. Moreover, even where the composition was significantly different, as for Pellets 44 and 49, the resulting deposits in the vents were more similar than between Capsules 44 and 45. It is possible that the significantly reduced material transport observed in Capsule 45 was due to a higher oxygen activity of Pellet 45 resulting from lack of vacuum outgassing. Work reported by Battelle Columbus Laboratories in 1973⁶ on mass transport within encapsulated MHW fuel points out that increased oxygen activity not only increases vaporization of Ir as IrO_3 , it is expected to decrease the vaporization of volatile impurities such as Ca, Si, Fe, Cr, and Ni (Al was not mentioned specifically in the Battelle report, but should behave in an analogous way to the other cations). The decrease in volatility with increasing oxygen pressure should be generally true for these cations whether they are present as binary, ternary, or higher compounds as long as they are present as oxides.

Recent work at SRL³ on the effect of atmosphere on impurity retention showed that heating PuO_2 doped with Ca, Al, Si, and P in vacuum at 1500°C removed more than twice as much by weight of the impurities than heating in flowing oxygen for the same length of time at the same temperature. Since the oxygen was flowing, the vapor species above the samples would be effectively removed in both cases. Hence, the different loss rates would be due more to differences in oxygen activity rather than evaporation kinetics. Si was found to volatilize more readily than either Ca or Al.

In the present study, Ir transport was only noticeable in the vent of Capsule 48 which had been outgassed. However, deposits of vaporized elements were present in all capsules, suggesting that vaporization of impurities from the fuel is more important to control than vaporization of Ir from the cladding. The analysis of the effusate on Capsule 49 suggests the same. The effusate had large amounts of Ir and W (Table 3). However, the major constituent was PuO_2 . Large amounts of Ca, Al, and Th were also present. Hence, even though vaporization of Ir occurred, vaporization of the fuel and its impurities was much greater (the fuel had >600 ppm Th).

From the results of this study as well as the results of the other two studies cited it appears that a final vacuum outgassing step may aggravate vent plugging. The evidence of these studies suggests that a better regimen for post hot pressing heat treatment

would be to give pellets a 6 hour vacuum outgassing immediately after hot pressing and follow this with a low temperature (700°C) final treatment in oxygen. The high temperature vacuum outgassing would reduce impurity levels and enlarge grain size with minimum crack growth; the low temperature oxygen heat treatment would burn off carbon from the die and restore stoichiometry to enhance the oxygen activity in the CVS. Preliminary work by SRL and SRP has shown that low temperature reoxidation does not lead to the same degree of pellet cracking as high temperature reoxidation. This change could only be implemented in future programs after additional study and impact testing.

The above interpretation for the differences in vent plugging is not unanimously shared by members of the heat source community. It has been pointed out, for example, that some of the MHW fuel sphere assemblies had plugged vents after aging, but had not been vacuum outgassed prior to aging. Statistics of the present study are too limited to permit demonstration of any mechanism. However, this study was designed to compare the results of each encapsulated pellet against the others. The fabrication histories and chemistry of all of the components have been investigated and the aging conditions were as similar as possible. Hence it is more valid to make comparisons among the present fueled capsules than among the present capsules and other clad fuel for which their fabrication histories are not well understood. The apparent conflicts point to a need to do repeat controlled compatibility studies to provide enough statistics to establish a mechanism.

Conclusions

Vent plugging has been a major concern of the heat source program, although, with one exception, none of the vents have plugged tightly enough to cause swelling of the iridium capsule. Multi-hundred watt (MHW) test fuel sphere assemblies were found to emit decay helium in bursts rather than continuously which suggests intermittent plugging. The one GPHS capsule vent test performed (ECT-1), also showed intermittent plugging in which the vent plugged, reopened, plugged again, and then reopened. The results of the present study provide evidence that the vent of Capsule 48 may have been plugged. Capsules 44 and 49 had extensive deposits and could have been or did become plugged. The microprobe work of the present study suggests that the intermittent gas release from the vents is caused by formation of a liquid phase in the filter element. According to this hypothesis, the liquid phase could accumulate until it filled the vent and blocked release of decay helium. The internal pressure could then build up until it blew a channel through the liquid phase and vented the helium. The present study shows that vent plugging is a function of the impurities in the fuel and the possibility of this occurrence might be minimized

by reducing the impurities in the fuel. This study also provides evidence that vent plugging may possibly be prevented by increasing the oxygen activity. Hence, the present work suggests that vacuum outgassing of pellets as a final heat treatment may not be as beneficial as originally expected.

Another major concern of Ir/PuO₂ compatibility is the effect of aging at elevated temperatures on the mechanical properties of the DOP-26 Ir. The present study confirms that aging Ir in the presence of PuO₂ leads to enhanced grain growth over aging of the Ir alone, especially of near-surface-grain (NSG) next to the fuel. Vent cups were especially susceptible to enhanced grain growth. ORNL⁷ has established that a major mechanism for grain growth is loss of Th from the Ir by oxidation of the Th at the surface. For enhanced growth of the near-surface-grains (NSG) like that seen in the cups of this study during aging for six months at 1330°C, an oxygen pressure of 10⁻⁵ torr was necessary to remove enough Th to cause the enhanced grain growth. The present study also shows evidence correlating growth of the NSG to loss of Th. Other effects may contribute to grain growth, but assuming Th depletion to be the primary cause, a key question to answer is the mechanism by which the fuel leads to Th depletion in the Ir. It is evident from the control samples of this study that the oxygen pressure was less than 10⁻⁵ torr since very little growth of the NSG was observed. It is expected that the graphite containers in which the samples were aged would maintain an oxygen pressure of about 10⁻⁹ torr at 1310°C Ir temperature. If the Th loss is due to oxygen pressure, then it is evident that the partial pressure of oxygen above the fuel within the capsule is greater than the partial pressure of oxygen outside the capsule. The results of the compatibility study also indicate that grain growth was greater for Capsule 49 which had much higher levels of impurities in the fuel. This would suggest that the impurities raised the internal oxygen pressure in the capsule if reaction with the Th at the Ir surface is controlled by oxygen pressure. However, it has been suggested that diffusion of the Th to the surface along grain boundaries, not oxygen pressure, is reaction rate controlling at the oxygen pressures expected in the capsule. If this is true, then the action of the impurities such as Fe and Cr which were found in large amounts on the grain boundaries may be to enhance Th diffusion. On the other hand, the impurities on the grain boundaries may act independently of the Th to cause grain growth by some mechanism such as changing interfacial energies.

The change in grain boundary chemistry observed in this study is expected to have some effect on impact ductility of the Ir apart from questions of grain size. The addition of Fe and Cr to the grain boundaries and the loss of Al associated with that addition is bound to have some affect on grain boundary cohesion and dislocation motion. However, how the ductility has been changed is not known.

The results of the Ir/Pu compatibility study also show that the impurities in the fuel have the following effects:

- Enhanced Pu escape from the CVS.
- Enhanced possibility of Ir crack initiation near the vent hole through formation of brittle Ir-Si intermetallics and very large grains (one to two grains per thickness).
- P levels normally present in the fuel show no evidence of producing deleterious effects in the fueled clads. We feel that phosphorus concentration in the fuel should not exceed about 15 ppm.

Recommendations

The results of this study led to several recommendations which should be considered by the heat source community for future research and production programs. Implementation in the current program is not possible because production of fuel is almost completed. Impurity reduction has not been shown to significantly enhance fuel quality, but may be desirable in the future to further ensure reliability.

Even though the GPHS fuel is expected to perform acceptably, the present study demonstrates that impurities in the fuel can affect the performance of the CVS. Hence, it is recommended that Ca, Al, and especially Si concentrations in the fuel be reduced to as low as practical in future heat source programs. To do this in the short term and to minimize the effects of the impurities that remain in the fuel, it is felt that the current final heat treatment oxygen and vacuum outgassing steps could be reversed. This recommendation would have to be tested before implementation. The new regimen would have the pellets be vacuum outgassed for 6 hours at 1500°C and then heat treated in oxygen at 700°C for approximately two hours (the exact time to be determined). The effect of oxygen activity on the RTG thermoelectrics would have to be assessed. The current specifications for Si, Ca, and Al for the PuO₂ feed are: Si, 200 ppm; Ca, 300 ppm; Al, 150 ppm. The measured concentration of these elements are typically less than 100 ppm, but one or more of these exceed this limit in greater than 50% of the powder batches. Since concentrations of a few hundred ppm of these elements show signs of second phase formation in the fuel (HF-2 from ECT-1 and Pellet 49 from the current study) which leads to vent plugging, a reduction in impurity level would be desirable, but not necessarily practical. Fueled capsules for which the PuO₂ has a Ca, Al, or Si content greater than about 100 ppm could enhance deposits in the vents if they have been stored at elevated temperatures for several months. For the longer term, we

recommend that a cost/benefit study be made on ways to reduce these elements to the lowest practical level. Since the actual levels to which these impurities should be reduced is not known, it is recommended that a study of the thermochemistry of these impurities in the PuO_2/Ir system be made. This study would identify the vapor species and vapor pressure of these species at different temperatures and oxygen activities as a function of storage time. These results would then be correlated with the observed build up of deposits in vents of CVS's heated under controlled conditions of temperature and oxygen activity (for example, with and without vacuum outgassing). As part of this work the reaction between Th and impurity vapor species would be investigated to help understand the cause of the Th depletion observed in the present study.

Fe, Cr, and Ni migrate from the fuel to the Ir cladding and alter the chemistry of the near-surface-grains and grain boundaries. Although the effect of these impurities is not now known, they should probably be excluded from the iridium until their effect is understood. The current specification for these impurities in the fuel is relatively high: Fe, 800 ppm; Cr, 250 ppm; Ni, 150 ppm. Although the compatibility study did not provide information on what the maximum concentration of these impurities in the fuel should be, it is felt that they should be as low as practical. We recommend that additional work be performed to establish the effect of different concentrations of Fe, Cr, and Ni on the impact ductility of DOP-26 Ir. These tests should specifically study the interactions of Th with Fe and Cr. If the test showed these elements degrade the iridium, then further work should be directed at determining the maximum concentration of these elements permissible in the fuel in order to maintain the impurity level in the Ir below the critical value.

The PuO_2 currently produced by SRP is optimum for the existing equipment and process. Any significant reduction in impurity level in future programs will require extensive studies in precipitation chemistry and powder processing. A capital investment program in processing equipment will be necessary. In order to make a reduction in impurities program meaningful, improved analytical techniques and equipment will have to be available for future heat source programs.

SURFACE AREA MEASUREMENTS OF $^{238}\text{PuO}_2$ USING THE BLAINE AIR PERMEABILITY APPARATUS

Introduction and Summary

The surface area of ceramic powder is a critical property in determining the response of the powder to temperature and pressure during forming of the powder into a ceramic body. A higher surface area results in a more reactive or "sinterable" powder. Final density, and pore and grain size distribution of the resultant body can also be affected. In an effort to characterize differences in PuO_2 feed powder batches used to fabricate hot-pressed fuel pellets in PuFF, a method of measuring surface area was investigated. It was hoped to be able to correlate some property of the feed, such as surface area, with fracture behavior of the hot-pressed fuel pellets. Measurement of surface area of $^{238}\text{PuO}_2$ by conventional BET methods is not possible because the self heating of the powder alters the adsorption of nitrogen upon which BET measurements depend. Another technique, Blaine air permeability (ASTM Standard Test C 204 - 79a), has been successfully adapted to measuring surface areas of $^{238}\text{PuO}_2$ powders. A modification of the Blaine technique was developed to permit using samples as small as one third the size called for in the standard test. This is especially useful when handling fissile or other hazardous materials that have inventory limits in process areas. Although the surface area was shown to be a more sensitive index of differences among $^{238}\text{PuO}_2$ powders than particle mode size (mode size is the particle size range having the largest population of particles as determined by Coulter counter), no correlation between it (surface area) and fracture tendency of the pellets was found for the feed lots and pellets tested.

Discussion

Experimental

The details of the Blaine method are explained in the ASTM standard. Briefly, the test consists of measuring the time required to pass a fixed volume of air (as measured by a manometer) through a plug of the test powder compacted into a cell of known volume. The volume of the cell is fixed by the length of the plunger used to compact the powder. The surface area is then calculated by comparing the measured time to the time required for an NBS standard cement powder of known surface area. Hence the Blaine surface area is a relative measurement rather than an absolute one. The surface area is calculated from the equation:

$$S = \frac{S_s \rho_s (1-e_s) \sqrt{n_s} \sqrt{e_s^3} \sqrt{t}}{\rho (1-e) \sqrt{n} \sqrt{e^3} \sqrt{t_s}} \quad (1)$$

Where:

- S = specific surface of the test sample, cm^2/g ,
 S_s = specific surface of the standard sample used in calibration of the apparatus, cm^2/g ,
 t = measured time interval for manometer drop for test sample,
 t_s = measured time interval for manometer drop for standard sample,
 n = viscosity of air, poises, at the temperature of the test sample,
 n_s = viscosity of air, poises, at the temperature of test of the standard sample used in calibration of the apparatus,
 e = porosity of prepared bed of test sample,
 e_s = porosity of prepared bed of standard sample used to calibrate the apparatus,
 ρ = crystal or theoretical density of test sample,
 ρ_s = theoretical density of standard sample.

Porosity is calculated from the equation

$$e = 1 - \frac{W}{V\rho} \quad (2)$$

where,

W = weight of the test sample, g

V = volume of apparatus into which the sample is compacted, cm^3 .

The NBS standard sample used to calibrate the apparatus is portland cement having the following properties as pertains to the Blaine:

$$\begin{aligned} S_s &= 3,500 \text{ cm}^2/\text{g} \\ \rho_s &= 3.15 \text{ g/cm}^3 \\ e_s &= 0.5 \\ t_s &= 100 \text{ sec} \end{aligned}$$

Substituting these into Eq. (1) we have (for samples at constant temperature)

$$S = 1557.2 \times \frac{\sqrt{e} \sqrt{t}}{\rho(1-e)} \quad (3)$$

Using Eq. (3), the Blaine surface area was determined for a variety of different powders.⁸ Samples of these powders were sent to Micromeritics Corp for surface area measurements by BET. With one exception, the two methods showed good agreement (Table 12). The exception note was probably due in part to break

TABLE 12

Surface Area - Measured by Blaine Fineness Tester and BET Methods

<u>Sample</u>	<u>Blaine, cm²/g</u>	<u>BET, cm²/g</u>	<u>Ratio</u>
KCl	256	145	0.57
K ₂ C ₂ O ₄ ·H ₂ O	357	9600	26.9
KNO ₃	539	311	0.56
Ce ₂ (C ₂ O ₄) ₃ ·9H ₂ O	3117	7244	2.3
Y ₂ O ₃	11,274	43,000	3.81
NBS Glass Beads	1805	1730 $\pm$ 50*	0.96

* Measured by National Bureau of Standards

up of the powder from slight heating during sample preparation for BET analysis.

Air permeability depends on the macro properties of the powders; that is, the shape of the pore channels through which the air permeates depends on the morphology of the particles. Since air cannot pass through them, the surface area of microvoids and pores in the particles cannot be measured. Hence the accuracy of the absolute measurement of surface area depends on the porosity of the particles. Because of this the Blaine method would not provide reliable absolute measurements of surface areas of agglomerates, etc. Nevertheless, measurements of relative "surface areas" of porous particles such as high fired PuFF shards would probably be helpful in detecting differences among batches of powders that would affect their processing behavior.

Small-Sample Modification of Blaine Apparatus

The ASTM standard Blaine apparatus has a specified cell volume into which the sample powder is compacted using a plunger of specified length. It is possible to obtain good results using smaller cell volumes. To do this it is convenient to use a series of progressively longer punches. A series of progressively sized punches is convenient not only from the point of view of being able to use smaller amounts of sample powder, it also greatly facilitates using the apparatus. For example, if a weighed amount of powder is too much or too little to pack properly in the cell volume defined by one punch, a different length punch can be used to get the correct compaction without having to add or remove sample, a laborious process for glove box work. For each punch used in the apparatus, the cell volume defined by that punch has to be measured according to the procedure defined by the ASTM standard.

When using nonstandard punches a correction factor must be applied to the result. The correction factor is equal to the ratio of the square root of the ASTM standard cell volume divided by the square root of the cell volume defined by the nonstandard punch. This correction factor was obtained in the following way. Eq. (3) shows that surface area is directly proportional to the square root of the time required to pass a fixed volume of air through the sample. However, for a smaller sample at the same porosity, the time would be less and the apparent surface area smaller. The true surface area is then

$$S_{\text{standard}} = S_{\text{nonstandard}} \times \frac{\sqrt{t_{\text{standard}}}}{\sqrt{t_{\text{nonstandard}}}} \quad (4)$$

where t_{standard} is the time for the sample in the standard cell volume. The time, t_{standard} , may not be known. However, as shown in Figure 24, the time for a fixed amount of air to be drawn through a sample plug of constant porosity in a cell of constant cross section is proportional to the weight of the sample which, in turn, is proportional to the cell volume being used. Hence,

$$\frac{S_{\text{standard}}}{S_{\text{nonstandard}}} = \frac{\sqrt{V_{\text{standard}}}}{\sqrt{V_{\text{nonstandard}}}} \quad (5)$$

As a test of Eq. (5), the surface areas were measured of six samples of Y_2O_3 powder. In addition to the standard cell volume, five smaller cell volumes were used as defined by a series of progressively longer punches (Table 13). Each sample was carefully weighed so that the porosity of the sample plug would be the same for each of the test cell volumes. As seen in Figure 24 the correction factor successfully converts the uncorrected "apparent" surface areas of the smaller cell volumes to the "true" surface area measured using the standard cell volume. The data suggest that the ratio of the square roots of the cell volumes gives slightly better results than the ratio of the square roots of the weights. Since the standard cell volume is known from the calibration of the apparatus, use of the cell volumes for the correction factor makes it possible to correct the apparent surface area from smaller samples without ever having to run a sample at the standard conditions.

As practical matter it is best to choose sample sizes large enough so that permeation times are large relative to the variation in times from repeat-measurements. Permeation times greater than about 45 seconds are usually adequate.

The best accuracy and reproducibility are obtained if powders are always compacted to the same bulk density. This is facilitated by using a series of punches that progressively differ in length by no more than about 1 mm graduations. In this way the samples can be quickly compacted at about the same pressure (which for the same powder usually adequately reproduces the same bulk density) without removing or adding powder.

Surface Area of PuO_2 Feed Powders

The surface areas of six samples of production feed powder were measured using the Blaine air permeability technique. Duplicate samples were run with good reproducibility achieved

TABLE 13

Punch Lengths and Cell Volumes for Small-Sample Modification Test

<u>Punch I.D.</u>	<u>Punch Length, mm</u>	<u>Cell Volumes, cm³</u>
Standard	45.97	1.8612
A-1	49.07	1.4791
A-2	52.27	1.0951
A-3	53.72	0.8977
A-4	55.22	0.6971
A-5	57.86	0.3505

FIGURE X. Surface Area of Y₂O₃ Test Powder
Using Small Sample Technique

24

Figure 24

Surface Area of Y_2O_3 Test Powder
Using Small Sample Technique

○ = SURFACE AREA VS WEIGHT CORRECTED BY RATIO OF SQ
△ = SURFACE AREA VS WEIGHT CORRECTED BY RATIO OF SQ

Sample Technique
Y₂O₃ Test Powder

EA VS WEIGHT CORRECTED BY RATIO OF SQUARE ROOTS OF VOLUMES
EA VS WEIGHT CORRECTED BY RATIO OF SQUARE ROOTS OF WEIGHTS

in each case. Sample sizes ranged from 4.0 to 4.6 g (relative density between about 0.20 and 0.25 g/cm³). Both the standard punch and punch A-1 (Table 13) were used. The heating effect of the Pu-238 was compensated for by estimating the temperature from the feel of the cell and multiplying the surface area by the ratio of the square roots of the viscosities as shown in Eq. 1. The viscosity of air at ambient temperature (22°C) is 1.818×10^{-4} poises. The viscosity of air at the estimated sample temperature (54°C) is 1.958×10^{-4} poises. Hence $S_{54^\circ\text{C}} = 0.963 S_{22^\circ\text{C}}$. The results (Table 14) showed a variation in surface area among these samples of up to a factor of two. In the overall spectrum of feed powder, larger variations probably exist. A series of pellets was made solely from each of the lots represented by the surface area samples. Separations Technology found no correlation between the number of integral or encapsulated pellets and the Blaine surface area (Table 14). However, a difference in surface area of a factor of two would be expected to have differences in processibility. Two tests are important in verifying that the surface area of the feed does not correlate with pellet yield. The first test would be to check the batch-to-batch surface areas of each batch in a lot. If large variations exist, then correlations could not be made between pellet yield and surface area based on one sample from one batch of the lot. The second test would be to measure the surface areas of several batches after each processing step in the PuFF flowsheet. The Blaine method would be especially useful to measure how much differences in feed powders transfer through ball milling. It is expected the method would also be successful in measuring differences in shards, especially high fired shards. If differences in surface areas do not transfer through ball milling then differences in feed powder may likely not be the cause of variations in pellet yield.

Table 14 also compares measured surface area to particle mode size. It is clear that surface area is a more sensitive index of powders than mode size since the differences in the reported mode sizes of the powders are not as large as the differences in surface areas.

Recommendations

The two tests mentioned above should be performed to track how far into the flowsheet significant differences in feed powder surface area are carried. It would be valuable to know as early as possible in the flowsheet when feed powders do not meet specifications for production of good pellets. If routine monitoring of feed powders by the Blaine method is attractive, the method can be somewhat automated to produce as many as 10 or more analyses per day. This would be done by using a long plunger driven by an electromechanical pressure device. The depth of the plunger would

TABLE 14

Surface Areas and Mode Sizes of Feed Powder Lots Versus Pellet
Yield

<u>Lot No.</u>	<u>Surface Area, cm²/g</u>	<u>Mode Size, μm</u>	<u>Yield, %</u>	
			<u>Encapsulated</u>	<u>Intergal</u>
585	4400 $\pm$ 59	5.58	86	50
586	6660 $\pm$ 306	5.98	79	50
587	4470 $\pm$ 59	--	100	86
588	3700 $\pm$ 68	5.72	100	100
590	4000 $\pm$ 216	4.99	56	44
591	3070 $\pm$ 59	4.74	17	17

be measured by a linear transducer. This configuration would allow any size sample to be compacted quickly to the desired density.

The equipment used to carry out this experimental program is available to SRP for use by Separations or Separations Technology in production. One apparatus is inside a glove box in the AMF and would have to be removed and packaged for contaminated shipment. A spare apparatus was built which has not been contaminated and is available immediately.

HELIUM RELEASE FROM $^{238}\text{PuO}_2$

Introduction

Helium accumulates in the $^{238}\text{PuO}_2$ lattice as the result of radioactive decay by emission of alpha particles. At high temperatures, such as those experienced by General Purpose Heat Source (GPHS) pellets during service and storage conditions, the helium is driven out of the lattice and accumulates on grain boundaries and in pores where it can weaken the microstructure. Under some conditions the build up of helium can lead to disintegration of the pellet. Studies have been done at both LANL and SRL to understand the mechanisms and conditions for release of helium from the PuO_2 lattice.^{9,10} These studies have shown that release of helium is primarily a function of temperature, but that the damage caused to the microstructure depends on many factors such as age of the pellet (helium inventory), heating rate, grain size, bulk density, fabrication history, and time at temperature. Helium damage can take the form of grain boundary bubbles, grain boundary separations or pore agglomeration. Work at SRL¹⁰ has suggested that approximately a six month inventory of helium is necessary before any effects on the microstructure are noticeable. If samples are heated to high temperatures at less than six month intervals, the SRL studies showed helium damage was minimal compared to samples that had been stored beyond six months and then heated. In addition, studies at both SRL and LANL^{9,10} indicate that a threshold temperature between 1150 and 1200°C is required before helium begins to migrate from the lattice into sinks such as grain boundaries and pores. The purpose of the helium release work has been to establish conditions for helium release that would minimize microstructural damage to the PuO_2 . The objectives of the current study were to (1) assess the helium damage to GPHS production type pellets as a function of time of storage at room temperature and subsequent firing temperature; and (2) determine the effectiveness of "dumping" the helium inventory at five month intervals on eliminating helium damage to pellets that required long term storage.

Summary

Helium effects were probably not present in the microstructure of PuO_2 pellets aged 4-6 months for post-aged heatings up to 1400°C. Grain boundary strain, evident as a tendency to over etch, occurred at temperatures of 1500 and 1600°C. For pellets aged 12 months, evidence suggests that on heating to 1100°C some helium may accumulate in pores and grain boundaries, possibly from the near surface regions of the lattice. At 1200°C, evidence of grain boundary decoration seen in the sample heated at 1100°C has disappeared suggesting some redistribution of the helium along the

grain boundaries has occurred permitting the grain boundary separations to close up. At 1300°C grain boundary separations in dense shards were visible. At 1400°C grain boundary effects had given way to marked pore agglomeration which at 1500°C had progressed to extensive separation of the shards themselves. At 1600°C the internal helium pressure appeared to drop permitting healing of the shard separations to take place.

Results for samples aged 24 months were available only for samples heated at 1300 and 1600°C. The samples heated at 1300°C had pore agglomeration similar to the sample aged 12 months and heated at 1400°C. The samples heated at 1600°C showed severe shard separations similar to the 12 month aged samples heated at 1500°C. Evidently the time at temperature for these samples was not long enough to exhaust the helium inventory and permit healing of the separations to commence.

In the periodic heating experiment, dumping of the helium inventory at 5 month intervals did not appear to effect the helium damage compared to control samples that had been stored without intermittent heating.

This study suggests that 1200°C is probably a near-optimum operating temperature with respect to minimizing helium damage. Temperatures above 1300°C can lead to significant pore agglomeration which could alter the impact behavior of the pellet.

Discussion

Experimental

Two pellets (No's. 30 and 32) made in the Plutonium Experimental Facility (PEF) according to the production flowsheet were selected for their as-fabricated microstructural homogeneity. Each pellet was made by hot pressing at 2800 psi and 1525°C followed by heat treating in Ar-5% O₂ at 1525 for 6 hrs. Pellet No. 30 was cut into approximately 41 pieces for use in the age versus temperature experiment. The pieces were stored separately at ambient temperature. After the designated storage time each sample was heated to the required temperature according to the matrix given in Table 15. The heatings were done under argon using a 300°C/hr heat up rate and a three hour hold at temperature. For comparison, a few samples were heated rapidly to 900°C and then heated at only 30°C/hr to temperature. Pellet 32 was cut into pieces for use in the intermittent heating experiment. Each test piece (Table 16) was heated to 1400°C at a rate of 300°C/hr and held at temperature for 24 hours to ensure removal of as much helium as possible.

TABLE 15

Test matrix for determining age and temperature threshold for helium induced damage. Pellet heated at temperatures given in Ar using 300°C/h heat ramp and 3 h hold at temperature. Samples cut from pellet 30 which was hot pressed at 280 psi and 1525°C on May 15, 1980 and heat treated in Ar-5% O₂ at 1525°C for 6 h on May 10, 1980.

Sample Age (Month)	Rt	1100	1200	1300	1400	1500	1600
4	-	9-9-80	9-25-80	9-11-80	9-26-80	10-4-80	10-10-80
4-6	-	11-17-80	11-20-80*	12-8-80	12-9-80	11-25-80*	11-14-80
6			1-10-81**			1-10-81**	
12	22 months	6-24-81	6-26-81	6-29-81	6-30-81	7-1-81	7-2-81
12 heat at 30 C/h above 900 C.					7-20-81	7-23-81	
24	24 months	6-29-82	6-28-82	6-24-82	6-23-82	6-30-82	7-6-82
24 heat at 30 C/h above 900 C.				7-8-82	7-7-82	7-14-82	7-14-82

* Pieces of pellet 32 heated by mistake. They are only 4 months old.

** Pieces of pellet 32 now 6 months old.

TABLE 16

Test matrix for determining helium effects of intermittent release of helium by heating at regular intervals at 1400°C for 24 h argon with a heating rate of 300°C/h. Samples cut from Pellet 32 which was hot pressed at 2800 psi and 1525°C on 1 July 1980 and heated in Ar-O₂ @ 1525°C for 6 hr on 10 July 1980.

Sample No.	Storage Temp. R.T.	Storage Time, Months			
		5	10	15	20
1	X	H* 12-23-80	H-E** 6-23-81		
2	X	-	H-E 6-23-81		
3	X	H 12-23-80	H 6-23-81		
4	X	-	-	H-E 10-6-81	
5	X	H 12-28-80	H 6-23-81	H 10-6-81	H-E 3-3-82
6	X	-	-	-	H-E 3-3-82

* H - Heated

** H-E = Heated and Examined

Results

Age Versus Firing Temperature

In the first experimental series, aging versus firing temperature, no helium damage could be confirmed in pellets aged 4 months until the firing temperature reached 1500°C (Figures 25 to 31). Grain boundaries of pellets fired at 1500 and 1600°C (Figures 30 and 31) for 6 hrs etched very rapidly compared to pellets fired at lower temperatures. Rapid etching has been attributed in other studies to helium induced grain boundary strain.⁹ Rapid etching of grain boundaries also occurred for samples aged 6 months and heated at 1500 and 1600°C (Figure 32). Pellets fired between 1200 and 1400°C revealed bubbles on the grain boundaries similar to those observed in other helium release experiment^{9,10} (Figures 33 to 35). No data is available for 100°C because the wrong sample was inadvertently heated in its place.

The most pronounced helium release effects were observed for pellets aged 12 months (Figures 36 to 46). In this 12 month series, pore agglomeration and grain boundary separations were observed in the unheated control sample when compared to an unaged sample of the same pellet (Figures 36 and 37). However, this sample was actually 22 months old when examined. The mechanism for this to occur at ambient temperature is unclear. Perhaps sufficient helium is released into the pores from the near-surface regions surrounding the pores. When 12 month old samples were heated at 1100°C, pore agglomeration appeared greater than for the control sample (Figure 38). Small, elongated pores were also apparent decorating grain boundaries in the as polished condition (Figure 38b, c). These elongated pores might be caused by migration of helium from the disturbed lattice making up the thickness of the grain boundary into the grain boundary itself. At 1200°C the pores decorating grain boundaries disappeared (Figure 39), possibly due to a redistribution of helium along the grain boundaries, although other studies have shown precipitation of bubbles at grain boundaries begins between 1150 and 1200°C. In these other studies the presence of grain boundary bubbles only appeared on etched samples. In the present study an etched sample of the specimen heated to 1200°C was unavailable. Additional pore coarsening may have occurred in the 1200°C sample. At 1300°C grain boundary separations and bubbles in dense shards were visible in as polished samples (Figure 40). The reappearance of grain boundary separations and pores is probably due to arrival of significant quantities of helium from the bulk material. Pore agglomeration was not obviously greater. At 1400°C, bubbles and separations were minimal even on etched grain boundaries (Figure 41). However, pore agglomeration was markedly greater. Evidently migration of helium away from grain boundaries and into pores occurs faster than arrival of helium to the boundaries. Pore coarsening appears to be even

FIGURE 1. As-Polished Microstructure; Stored 4 Months and Heated at 1100°C.
23 (a) and (b) Typical pore distribution; (c) Higher magnification of (b).

a

b

FIGURE 2. Etched Microstructure After 4 Months Storage and Heating to 1100°C (Etched 1/2 hr).
20

- 83 -

a

b

c

FIGURE 3. Microstructure After Storing 4 Months and Heating at 1200°C for 3 Hrs.
27 (a) and (b) As-Polished; (c) Etched 1/2 hr.

FIGURE 4. Microstructure After Storing 4 Months and Heating at 1300°C for 3 Hrs.
 28 (a) and (b) As-Polished; (c) Etched 1/2 hr.

a

b

c

FIGURE 8. Microstructure After Storing 4 Months and Heating at 1400°C for 3 Hrs.
29 (a) As-Polished; (b) and (c) Etched 1/2 hr.

FIGURE 8. Microstructure After Storing 4 Months and Heating at 1500°C for 3 Hrs.
30 (a) and (b) As-Polished; (c) Etched 1/2 hr.

a

b

FIGURE 7. Microstructure After 4 Months Storage and Heating at 1600°C for 3 Hrs.
31 (a) As-Polished; (b) Etched 1 hr.

a

b

c

FIGURE 32. Microstructure After 6 Month Storage and Heating at 1500°C for 3 Hrs.
(a) and (b) As-Polished; (c) Etched 1 hr.

³³
FIGURE 9. Microstructure After 6 Month Storage and Heating at 1200°C for 3 Hrs.
(a) and (b) As-Polished; (c) Etched 1 hr.

a

b

c

FIGURE ³⁴~~10~~. Microstructure After 6 Month Storage and Heating at 1300°C for 3 Hrs.
(a) and (b) As-Polished; (c) Etched 1/2 hr.

a

b

c

d

35
FIGURE 11. Microstructure After 6 Month Storage and Heating at 1400°C for 3 Hrs.
(a) and (b) As-Polished; (c) and (d) Etched.

a

b

c

FIGURE ³⁶₁₂. Microstructure After Storing 22 Month at Room Temperature. Some Grain Boundary Separation has Occurred. As-Polished.

d

e

36
FIGURE 12. Continued (d) and (e) Detail of Grain Boundary Separation.
As-Polished.

- 74 -

37
FIGURE 13. Microstructure of Unaged Control Sample (a) Quarter Section of Pellet; (b) and (c) Typical pore Distribution (As-Polished).

-95-

a

b

c

³⁸
FIGURE 14. Microstructure After Aging 12 Months and Heating at 1100°C for 3 Hrs.
(As-Polished).

--96--

a

b

c

FIGURE ³⁹~~15~~. Microstructure After Aging 12 Months and Heating at 1200°C for 3 Hrs. (As-Polished).

a

b

FIGURE 40
16. Microstructure After Aging 12 Months and Heating to 1300°C for 3 Hrs (As-Polished).

c

d

⁴⁰
FIGURE 16. (Continued) Microstructure After Aging 12 Months and Heating at 1300°C for 3 Hrs. (c) As-Polished, showing Grain Boundary Separations and Bubbles; (d) Etched.

41
FIGURE VI. Microstructure After Aging 12 Months and Heating at 1400°C for 3 Hrs.
(a) and (b) As-Polished; (c) Etched.

- 100 -

a

b

c

⁴²
FIGURE 18. Microstructure After Aging 12 Months and Heating to 1400°C at a Rate of 30°C/hr Instead of 300°C/hr. Time at Temperature = 3 Hrs.

- 101 -

a

b

c

FIGURE ⁴³19. Microstructure After Aging 12 Months and Heating at 1500°C for 3 Hrs. (As-Polished).

44
FIGURE 20. Microstructure After Aging 12 Months and Heating to 1500°C at a Rate of 30°C/hr Instead of 300°C/hr. Time at Temperature = 3 Hrs (As-Polished).

d

e

44
FIGURE 20. (Continued) Microstructure After Aging 12 Months and Heating to 1500°C at a Rate of 30°C/hr. Grain Boundary Etched.

a

b

c

FIGURE 45 ~~41~~. Microstructure After Aging 12 Months and Heating at 1600°C for 3 Hrs (As-Polished).

HEATED AT 1100 C FOR 3 HRS

LITTLE EFFECT

HEATED AT 1500 C FOR 3 HRS

MAXIMUM EFFECT: SHARD SEPARATION

HEATED AT 1600 C FOR 3 HRS

HEALING

⁴⁶
FIGURE 22. Effects of Helium on Microstructure for Samples Aged 12 Months.

greater for the sample heated at 30°C/hr (Figure 42). At 1500°C, pore agglomeration was severe (Figure 43). Grain boundary bubbles and separations were not noticeable on polished samples as they had been on samples heated to 1300°C. An unusual effect of heating at 30°C/hr was observed (Figure 44). Instead of enhanced particle separation, the slower rate resulted in a more homogeneous distribution of smaller, more uniformly sized pores. At 1600°C extensive healing of particle separations in the microstructure had taken place suggesting that the helium inventory in the lattice had been exhausted and gas in the pores had been expelled (Figure 45). The sequence of pore agglomeration, particle separation and subsequent healing observed for the 12 month aged samples is summarized for clarity in Figure 46.

Looking at Figure 43, there is doubt whether the pore structure, being so open, could be caused by gas pressure. It may simply be thermal coalescence of residual pores left by the gas after it has escaped.¹¹ However, even open microstructures can sustain large gas pressures if the internal gas generation rate is high relative to the rate of escape of the gas along pore channels. That this might have been the case at 1500°C is suggested by Figures 43 and 44. The microstructure of Figure 44 was generated by heating a sample from the same pellet as that shown in Figure 43 under the same conditions excepting that the sample in Figure 44 had a slower heat up rate. The slower rate would have allowed the ratio of gas escape to gas generation to be closer to one than for the higher heating rate.

Of the samples aged for 24 months, only data on the control sample and samples heated at 1300°C and 1600°C were available. As expected, the control sample (Figure 47) showed pore agglomeration similar to that for the 12 (but actually 22) month control sample (Figure 36) that was not heated. The samples heated at 1300°C (Figure 48) showed pore agglomeration similar to those 12 month aged samples heated to 1400°C (Figure 41). Samples heated at 300°C/hr had bubbles at the grain boundaries. Grain boundaries of samples heated at 30°C/hr revealed grain boundary separations, otherwise the microstructure was similar to the sample heated at 300°C/hr (Figure 49). This behavior contrasts within the 12 month/1400°C microstructure and suggests that the helium inventory was large enough to cause the same effect regardless of heating rate. The samples heated at 1600°C in this series showed considerable pore agglomeration (Figure 50). No effect of heating rate was apparent (Figure 51). When etched, these samples surprisingly had the herringbone pattern typical of reduced and etched PuO₂ (Figures 50c, e and 51c, d). It is difficult to explain this as reduction by argon at 1600°C since other samples heated under the same conditions did not show this effect. It is likewise difficult to ascribe this to helium since exhaustion of the helium inventory and healing of microstructural defects occurred in other samples

47
FIGURE 25. Microstructure After Aging 24 Months at Ambient Temperature.
As-Polished.

d

e

FIGURE ⁴⁷~~25~~. (Continued) Microstructure After Aging 24 Months at Ambient Temperature. Grain Boundary Etched.

a

b

c

⁴⁸
FIGURE 24. Microstructure After Aging 24 Months and Heated at 1300°C for 3 Hrs (As-Polished).

d

e

⁴⁸
 FIGURE 24. (Continued) Microstructure After Aging 24 Months and Heating at 1300°C for 3 Hrs (Grain Boundary Etched).

a

b

c

FIGURE 25. ⁴⁹Microstructure After Aging 24 Months and Heating to 1300°C at a Rate of 30°C/hr Instead of 300°C/hr. Time at Temperature = 3 Hr (As-Polished).

d

e

49
 FIGURE 25. (Continued) Microstructure After Aging 24 Months and Heating to 1300°C at a Rate of 30°C/hr Instead of 300°C/hr (Grain Boundary Etched).
 C.

⁵⁰
~~FIGURE 26.~~ Microstructure After Aging 24 Months and Heating at 1600°C for 3 Hrs.
(a), (b) and (d) As-Polished; (c) and (e) Grain Boundary Etched 1/2 hr.

a

b

c

d

51
FIGURE 21. Microstructure After Aging 24 Months and Heating to 1600°C at a Rate of 30°C/hr. (a) and (b) As-Polished; (c) and (d) Grain Boundary Etched 1/2 hr.

heated at this temperature. It is not clear how an inadvertent use of a reducing atmosphere would have been possible.

Intermittent Heating

No effect of dumping the helium inventory by heating at 5 month intervals was observed (Figures 52 to 54). In both the control samples (no periodic heating) and the test samples (periodic heating) pore agglomeration was evident. However, the microstructures were indistinguishable.

Conclusions

In terms of preventing helium induced changes in the microstructure, the results of this study confirm those of the LANL study that an operating temperature of about 1200°C is probably near optimum for pellets that have been allowed to build a large inventory of helium. Temperatures above 1300°C can lead to significant pore agglomeration which could alter the impact behavior of the pellet.

a

b

c

d

e

52
FIGURE 28. Effect on Microstructure of Intermittent Heating During Aging. (a) and (b) Aged 10 Months with 1 Intermittent Heating and a Final Heating at 1400°C for 24 hrs After 10 Months; (c), (d) and (e) Control Sample Aged 10 Months Then Heated at 1400°C for 24 hrs (See Table 2).

53
 FIGURE 29. Effect on Microstructure of Intermittent Heating During Aging (a), (b) and (c) Aged 15 Months with 2 Intermittent Heatings and a Final Heating at 1400°C for 24 hrs After 15 Months; (d), (e) and (f) Control Sample Aged 15 Months Then Heated at 1400°C for 24 hrs (See Table 2). As-Polished.

a

b

53
FIGURE 29. (Continued) Effect of Intermittent Heating
During Aging (a) Two Intermittent Heatings;
(b) Control. Etched.

54
 FIGURE 30. Effect on Microstructure of Intermittent Heating During Aging (a), (b) and (c) Aged 20 Months with 3 Intermittent Heatings and a Final Heating at 1400°C for 24 hrs After 20 Months; (d), (e) and (f) Control Sample Aged 20 Months Then Heated at 1400°C for 24 hrs. All Samples As-Polished.

g

h

SA
FIGURE 30. (Continued) Effect on Microstructure of Intermittent Heating During Aging (g) Three Intermittent Heatings, Etched 2 hrs; (h) Control, Etched.

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