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of 71 pages.

QUARTERLY PROGRESS REPORT
PLUTONIUM METALLURGY OPERATION
JULY, AUGUST, SEPTEMBER, 1962

By

The Staff of Plutonium Metallurgy Operation

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October 15, 1962

HANFORD ATOMIC PRODUCTS OPERATION
RICHLAND, WASHINGTON

Work performed under Contract No. AT(45-1)-1350 between the
Atomic Energy Commission and General Electric Company

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2.1

2.0 PHYSICAL AND MECHANICAL METALLURGY

Preliminary Investigation of the Effect of Specific Impurities on the Transformation Kinetics of Plutonium - G. A. Saltzman

Recent studies of the kinetics of the beta-alpha transformation in plutonium^(1, 2, 3) have produced differences in results attributed to a number of causes. The effect of impurities in the plutonium is thought to be one major cause. R. D. Nelson^(1, 2) has shown the effect of some general impurity concentrations on the time-temperature-transformation curve of the beta-alpha transformation.

This investigation shows the effect of some specific impurity additions to a high purity plutonium base by comparison of the time-temperature-transformation curves developed for each composition. The three metals added to the plutonium are commonly found as impurities and were randomly selected to begin this study.

The isothermal transformation was investigated at temperatures from -100 C to 85 C by means of isothermal reaction curves obtained using fluid displacement techniques.^(1, 2) The time-temperature-transformation curves were derived from series of these isothermal reaction curves.

Isothermal reaction curves obtained by this same method were used to observe the effect of alpha-beta-alpha cycling on the transformation rate. Each of three specimens was transformed isothermally at one temperature after a standard beta heat treatment. This was repeated three times.

Density measurements and metallography were the means used to observe the effect of the impurity additions on microcrack formation in cast metal and propagation of microcracks due to thermal cycling.

The effect of impurities on the kinetics of the beta-alpha phase transformation in high purity plutonium is more dependent on the nature of the impurity than on the amount of impurity when dealing with low (< 1000 ppm) impurity content. Of those impurity compositions investigated:

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1. The 1 and 50% transformation lines of the time-temperature-transformation curves, for the additions of 100 ppm nickel, 1000 ppm nickel, and 334 ppm iron to high plutonium, were almost coincidental with these lines for the high purity metal.
2. The 1 and 50% transformation lines of the partial time-temperature-transformation curve for the 600 ppm aluminum composition were close to those of the high purity metal at -100 C but became increasingly divergent with increasing temperature.

The effect of impurities on microcrack formation in as-cast plutonium, and on propagation of microcracks due to thermal cycling was observed by density measurements and metallographic study. For high purity metal, and the nickel and iron compositions, the following was observed:

1. In the as-cast condition, the high purity metal had the greatest number of microcracks, though they were quite small. The 1000 ppm nickel had the smallest amount of microcracks, with 100 ppm nickel and 334 ppm iron having a similar amount, intermediate with respect to the other two.
2. After thermal cycling between alpha and beta, ten cycles from 175 C to -10 C, the high purity plutonium had shown the greatest amount of void growth and density loss, followed in decreasing amounts of damage by the 100 ppm nickel, 1000 ppm nickel and 334 ppm iron.

The effect of alpha-beta-alpha cycling on the transformation rate was seen to be very great at -100 C, lesser at -23 C, and small but appreciable at 25 C. Specimens beta heat treated and isothermally transformed at each of these temperatures, showed a slower start and transformation rate with each of four repetitions; however, the time for completion did not seem to be greatly affected.

An as-reduced plutonium button having a density of 19.51 was obtained and remelted to produce the high purity ingot material used in this

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study. The impurity compositions were produced by melting the combined charge of ingot and impurity metal at 950 C in vacuo and pouring into a MgO-coated graphite mold heated at 350 C. The as-cast densities and impurity contents of the five compositions cast are shown in Table 2.1.

Wafers, 1-inch in diameter and 0.030 to 0.045-inch thick, were machined from the cast ingots. A small hole was drilled near one edge of the wafer to accommodate a 0.005-inch wire used in suspending the wafer in a liquid.

Specimens were weighed in air and in the isothermal bath at the temperature at which the transformation was to be carried out. They were heated in silicone oil under vacuum or in an argon atmosphere. A standard alpha-beta heat treatment, 160 C for 30 minutes, was used for all specimens. Isothermal reaction curves of the beta-alpha transformation were obtained by quenching from 160 C to temperatures between -100 and 85 C, and holding isothermally while recording weight of the suspended specimen as a function of time. Silicone oil was used as the quenching medium for temperatures above +20 C, carbon tetrachloride for -23 C, a freon for -50 C, and FC-75, an inert fluorochemical for -100 C.

Thermal cycling, to investigate the growth of microcracks, was carried out by cycling through the alpha-beta-alpha transformation. Ten cycles from 175 C to -10 C were carried out by holding in silicone oil at 175 C for 2 minutes, holding at room temperature in carbon tetrachloride for 1 minute, and holding in carbon tetrachloride at -10 for 2 minutes.

Isothermal reaction curves showing weight increase as a function of time are not shown. Figure 2.1-A is typical of these curves for the transformation somewhat above room temperature. The initial slope is produced by densification of metastable beta prior to the beginning of transformation. Figure 2.1-B is typical for room temperature and lower. Here the initial [redacted] may or may not have caught the transformation start.

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TABLE 2.1

DENSITY AND IMPURITY CONTENT OF AS-CAST PLUTONIUM
(ppm by weight)

Impurity Addition	<u>None</u>	<u>Low N_i</u>	<u>High N_i</u>	<u>Iron</u>	<u>Aluminum</u>
Density, 25 C	19.6549	19.6263	19.5811	19.5623	18.1874
Aluminum	13	- -	13	13	
Calcium	2	<2	50	50	
Carbon	25	260	1530*	600*	110
Chromium	- -	- -	10	10	
Copper	<1	2	2	5	
Iron	<50	<50	226	334	
Lead	<1	2	5	2	
Magnesium	10	10	50	50	
Manganese	10	10	20	20	
Nickel	5	100**	1000**	5	
Potassium	10	- -	5	20	
Silicon	10	5	2	1	
Sodium	50	1	20	50	
Tin	<1	1	- -	- -	

* Doubtful analyses

** Based on impurity addition

FIGURE 2.1

Typical Isothermal Reaction Curves as Plotted from Data

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Isothermal reaction curves, showing fraction transformed as a function of time, are shown for each composition. These appear as Figure 2.2 to 2.7. The fraction transformed was obtained from the relationship:

$$f = \frac{W_t - W_i}{W_f - W_i}$$

f = fraction of beta transformed to alpha

W_t = weight in isothermal bath at any time

W_i = initial weight in isothermal bath as extrapolated or interpolated

W_f = weight of alpha in isothermal bath prior to beta heat treatment

FIGURE 2.2

Isothermal Reaction Curves of Beta-Alpha Transformation
High Purity Plutonium

Figure Without Title Unclassified

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2.7

FIGURE 2.3

Isothermal Reaction Curves of Beta-Alpha Transformation
High Purity Plutonium

FIGURE 2.4

Isothermal Reaction Curves of Beta-Alpha Transformation
100 ppm Nickel Impurity

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(a)

(b)

FIGURE 2.5

Isothermal Reaction Curves of Beta-Alpha Transformation
1000 ppm Nickel Impurity

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(a)

(b)

FIGURE 2.6

Isothermal Reaction Curves of Beta-Alpha Transformation
334 ppm Iron Impurity

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2.10

FIGURE 2.7

Isothermal Reaction Curves of Beta-Alpha Transformation
600 ppm Aluminum Impurity
Figure Without Title Unclassified

Since structural damage takes place during the latter 50% of the beta-alpha transformation, (2, 3) the isothermal reaction curves are plotted from data and drawn as a solid line only to a point just above 50% transformed. The latter half of the curve is shown with the same general characteristics as that obtained from plotted data and carried to 100% completion at the time when there was no further increase in the weight of the suspended specimen.

From each series of isothermal reaction curves obtained, a partial time-temperature-transformation curve for each composition was developed. Some data obtained for temperatures below 23 C was later disregarded. This was due to the effect of cycling, described later, since a new specimen was not used for each transformation. Comparison of the 1% and 50% transformation lines, above 23 C, showed the kinetics of the transformation to be almost unaffected by the nickel and iron additions. The rate of transformation of the aluminum composition was

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2. 11

unaffected at -100 C, but became increasingly sluggish with increasing temperatures. Figure 2.8 shows the time-temperature-transformation (T-T-T) curve developed for the high purity metal. The major difference in this curve, as compared to those previously reported, (2, 3) is in a faster start and rate of 50% transformation at -100 C.

FIGURE 2.8

T-T-T Curve of Beta-Alpha Transformation
High Purity Plutonium

Figures 2.9, 2.10, 2.11 and 2.12 show the partial time-temperature-transformation curves developed for the 100 ppm nickel, 1000 ppm nickel, 334 ppm iron and 600 ppm aluminum compositions, respectively. Superimposed on Figures 2.9 to 2.12 are the 1 and 50% transformation lines from the high purity plutonium time-temperature-transformation curve, Figure 2.8. They are shown as dashed lines. Apparently, impurity elements having no solid solubility have little or no effect on the transformation kinetics.

Figures Without Titles Unclassified

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2.12

FIGURE 2.9

T-T-T Curve of Beta-Alpha Transformation
100 ppm Nickel Impurity

FIGURE 2.10

T-T-T Curve of Beta-Alpha Transformation
1000 ppm Nickel Impurity

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FIGURE 2.11

T-T-T Curve of Beta-Alpha Transformation
334 ppm Iron Impurity

FIGURE 2.12

T-T-T Curve of Beta-Alpha Transformation
600 ppm Aluminum Impurity

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A specimen of each composition, except the aluminum, was thermally cycled from 175 to -10 C, through the beta-alpha transformation, ten times. The effect of the iron and nickel impurities was compared on the basis of microcracks and voids prior to (in the as-cast condition) and after cycling, and on the basis of % decrease in density due to cycling. As can be seen in Table 2.2 the high purity plutonium had the greatest density loss.

TABLE 2.2

% DENSITY DECREASE OF VARYING COMPOSITIONS DUE TO
THERMAL CYCLING TEN TIMES BETWEEN 175 and -10 C

<u>COMPOSITION</u>	<u>DENSITY DECREASE (%)</u>
High Purity	6.20
100 ppm Nickel	4.38
1000 ppm Nickel	1.42
350 ppm Iron	1.20

The 100 ppm nickel, 1000 ppm nickel and 334 ppm iron had decreasing amounts of density loss. The effect of cycling on amount and size of microcracks is seen in Figure 2.13 which shows microcracks before cycling, in the as-cast condition, and after cycling.

These photomicrographs verify the density measurements. These results do not mean that increased impurity content lessens thermal cycling damage. They do seem to indicate that certain amounts of specific impurities lessen microcracks in cast high purity plutonium and decreases the extent of propagation of these microcracks when the metal is thermally cycled. This fact has been noted previously with respect to iron content. (4)

The effect of cycling a single specimen through an isothermal beta-alpha transformation and a repeated alpha-beta treatment is shown in Figure 2.14 to 2.16. Figure 2.14 shows the effect of repeating a beta heat treatment of 160 C for 30 minutes, and an isothermal transformation at -100 C on the beta-alpha transformation kinetics. The second cycle is greatly effected, and third and fourth cycles show increasingly slow starts.

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The completion may not be effected to any extent as seen more clearly in Figure 2.15. This figure shows the effect of the transformation at -23 C, Figure 2.16 shows the transformation at 25 C.

Some data obtained for specimens containing the iron and nickel impurities show a similar change in transformation kinetics, so this effect is not attributed to impurities. Stresses introduced may be the primary cause.

FIGURE 2.13

Photomicrographs Comparing Voids in Cast Structure with Those After Thermal Cycling Ten Times Between Alpha and Beta Phases
100X except (B), 250X

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2.16

HW 54512

(E)
8068 High Purity Plutonium
After Cycling

(F)
8069 100 ppm Nickel
After Cycling

(G)
8057 1000 ppm Nickel
After Cycling

(H)
8058 500 ppm Iron
After Cycling

FIGURE 2.13 II

Photomicrographs Comparing Voids in Cast Structure with Those After
Thermal Cycling Ten Times Between Alpha and Beta Phases.
100X

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2.17

FIGURE 2.14

Effect of Repeated Isothermal Beta-Alpha Transformations
at -100 C on the Isothermal Reaction Curve

FIGURE 2.15

Effect of Repeated Isothermal Beta-Alpha Transformations
at -23 C on the Isothermal Reaction Curve

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2.18

FIGURE 2.16

Effect of Repeated Isothermal Beta-Alpha Transformations
at 25 C on the Isothermal Reaction Curve

Nucleation and Growth Characteristics of Alpha Plutonium -

R. D. Nelson

An investigation was initiated to study the nucleation and growth characteristics of the beta-alpha transformation of unalloyed plutonium. The method of conducting the investigation was to interrupt the isothermal transformation after a certain fraction transformed and determine nucleation and growth parameters by observing the grain size and the number of grains formed. The characteristics of the transformation can also be observed metallographically. The growth parameter is determined by plotting the largest dimension of the largest grain as a function of time as measured from the start of the transformation.

The procedure employed was to beta heat treat the specimens for 1.5 hours at 170 C, quench to various isothermal transformation temperatures high in the alpha phase and follow the transformation by the fluid displacement technique, interrupt the transformation after the desired %

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transformed and quench to -40 C to complete the transformation. The grain structure of the alpha phase formed under the two thermal conditions was of markedly different structure thus permitting an analysis of the transformation at the higher temperature.

At this temperature (79) the alpha phase initially formed in bands of columnar grains with the largest dimension at right angles to the axis of the band, Figure 2.17. The alpha formed after quenching to -40 C are the small grains with irregular boundaries. In the specimens, having transformed 2.5 and 7%, the bands were observed to occur across the entire width of the specimens which were 1-centimeter diameter and 2-millimeters thick. Also, the grains appeared to nucleate and grow from a common interface, Figure 2.18.

The largest dimensions of the largest observed grain in each specimen was measured and plotted as a function of time from the start of the transformation, Figure 2.19. These data show that the grain size increased to a maximum value of 0.14 to 0.16 millimeter which occurred after 27% transformation. Beyond this, impingement occurred due to the rapid rate of nucleation, the parameter of which has not yet been determined. The slope of the initial portion of the curve, was 3×10^{-5} mm/sec and was the type of growth parameter desired.

Metallography - D. D. Hays

A Reichard Model MeF metallograph with a microhardness tester has been installed in the metallographic glove box train. The metallograph is equipped for polarized light, dark field and incident light investigations. Either a low voltage tungsten filament lamp or a high pressure mercury vapor lamp can be used as a light source.

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FIGURE 2.17

Microstructure Showing the Bands of Columnar Grains of the
Alpha Phase After 35% Transformation at 79 C
250X

FIGURE 2.18

Microstructure Showing the Interface Along Which the Alpha Grains
Appeared to Nucleate and Grow
250X

Photographs Without Titles Unclassified

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FIGURE 2.19

Maximum Grain Size as a Function of the Time from the Start
of the $\beta \rightarrow \alpha$ Transformation at 79 C
After Beta Heat Treating 1.5 Hours at 170 C

Figure Without Title Unclassified

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3.0 PLUTONIUM FUELS DEVELOPMENT

PRTR Fuels

Fuel Element Fabrication - R. E. Sharp

Fabrication continued during this period of uniformly enriched urania-plutonia ($\text{UO}_2\text{-PuO}_2$) fuel element rods for PRTR irradiation testing. Sufficient rods for 11 vibratory compacted and seven swage compacted 19-rod clusters were loaded with 0.48-wt % PuO_2 (nominal 16.5% Pu^{240}) in UO_2 . These rods are in the latter stages of fabrication (etching, autoclaving and wire wrapping) and will be assembled into clusters during the next quarter. When these fuel elements are assembled and the two or three clusters presently being loaded are completed it will exhaust the supply of 16.5% Pu^{240} material. This will make a total of 52 fuel element clusters fabricated containing 16.5% Pu^{240} . The next 20 clusters fabricated will contain 8% Pu^{240} material.

Fabrication Development

Oxide Fuel Development - R. E. Bardsley

A statistical analysis of swaging variables, aimed at improving swaged length control, was conducted by W. L. Lawton of Plutonium Metallurgy Operation with the support of the Applied Mathematics Operation. The study, based on data collected during the fabrication of over 600 fuel rods, provided information for a series of swaging tests. Utilizing this information, an initial test group of 12 rods have been fabricated, all of the rods meeting the predicted values. A second test consisting of 30 rods is now being prepared. These rods will represent three rods fabricated from each of ten tubing weight classes. The tubing length and core weight for each of these tubing weight classes will be closely controlled to meet the values provided by the statistical analysis.

Distribution studies using autoradiographic techniques have been conducted on both swage and vibrational compacted fuel rods. Test rods

have been loaded incrementally and vibrated (shaker table) for different durations at various amplitudes. Evaluation of these rods indicated that although the core quality had improved, it was not of the degree desired due to segregation within each individual increment. Additional rods have been loaded, and the autoradiographs are now being evaluated. These rods were again loaded by various methods which included:

1. Loading using 300 increments
2. "Bottle" loading - the total core material for one rod mixed in a container and poured into the tube
3. Loading incrementally, sealing, and vibrating on the vibrational compactor unit.

Extended Surface Plutonium Fuels - C. H. Bloomster

Two additional zirconium-clad, plutonium-zirconium alloy fuel plates were made by roll-cladding; as in the previous plate the aluminum foil wrapping used around the core for contamination control was eliminated. To minimize contamination which might occur during heating and early compaction of the "loose" assembly, the assembled sandwich was cold-rolled until the sandwich was tightly compacted. The plutonium core was thus "locked" in place to prevent movement of minute plutonium particles, which cause contamination. After cold-rolling the sandwiches were hot-rolled in the usual manner. The cold-rolling appeared partially successful. One plate was not contaminated and one plate had slight contamination on the edge. Both plates were sheared to within one-fourth inch of the core without encountering further contamination. The plates appeared to be well bonded.

A metallographic examination showed the core thickness to vary approximately 20% except at the edges and ends where the core was thinner. The thinning results from the extreme softness of the core alloy. It is believed that the thinning will not present a serious fabrication problem. The thinning may be accepted, the core or components preshaped, and the core hardened by alloying.

In a scale-up experiment, a 30 gram plutonium-zirconium core was roll-clad with zirconium, previous plates contained 10 gram plutonium cores. The bare plutonium-zirconium core was assembled in the zirconium picture frame, the steel sandwich welded shut, cold-rolled to compact the sandwich, and hot-rolled. The finished plate was bonded; however, widespread alpha contamination existed on the zirconium surface. The contamination was readily removed by etching except on the edge where an alpha count of 5000 dis/min existed. The contamination was nonsmearable but apparently rather general throughout the bond zone since it occurred in many locations and was not removed by abrading the contaminated areas. Further decontamination techniques are being tried on this piece. In addition, coating techniques will be tried on the core material in order to prevent contamination in the first place. It is planned to try copper and nickel plating and tin or zirconium foil wrappings. Aluminum foil wrapping previously used was successful in preventing contamination to the outside of the plate, but the aluminum apparently aided the formation of intermetallic compounds in the plutonium-zirconium core which in turn caused wide variations in the core thickness.

Irradiation Testing

Phoenix Experiment - M. D. Freshley and L. C. Schmid

The plutonium burnup experiment designed to investigate the effect of exposure on the reactivity of high exposure plutonium is continuing. Plutonium containing capsules are irradiated in the MTR and their reactivity is measured in the Advanced Reactivity Measurement Facility (ARMF). Three samples with plutonium of different isotopic compositions are being irradiated at a power generation of 49 kw/ft and a surface heat flux of about 1,000,000 Btu/(hr)(ft²).

Current status of the samples is as follows: the sample containing plutonium which initially had 6.25% Pu²⁴⁰ (GEH-21-1) has received 5 cycles

of irradiation and its reactivity has been measured in the ARMF; the sample containing plutonium with 16.33% Pu^{240} (GEH-21-3) has been irradiated for its sixth cycle; and the sample containing plutonium with 27.17% Pu^{240} (GEH-21-19) has been irradiated for 6 cycles and ARMF measurements have been completed. Goal exposure of these samples is 7 MTR cycles. Continuous reactivity measurements were started on GEH-11-3 within 6 hours after the MTR shutdown following its sixth cycle of irradiation. The purpose of this transient measurement is to determine the reactivity effect of the short-lived fission products. A similar measurement was made on the same sample following its first cycle of irradiation.

Preliminary data indicates that the sample which contains 27.17% Pu^{240} has about 5% more reactivity than the sample which contains 6.25% Pu^{240} after about 3 cycles of irradiation.

A calibration capsule for determining what effect the presence of an aluminum-plutonium Phoenix type sample has on the ARMF spectrum has been fabricated. The capsule consists of an aluminum-plutonium alloy sample enclosed in Zircaloy cladding. The capsule parts in the center and is normally held together by screwing the 2 halves into Zircaloy sleeves. Aluminum and cadmium activation foil containers are positioned between the 2 halves of the sample. The zirconium cladding which covers the ends of the aluminum-plutonium sample in the center of the capsule was made 0.005-inch thick in order to place the aluminum-plutonium sample as close to the activation foils as possible. Copper, gold, manganese, indium, and lutetium foils will be used for these measurements.

Oxide Capsules - W. J. Bailey and T. D. Chikalla

The capsule containing high density UO_2 -2.57 mole % PuO_2 (GEH-14-85) was discharged from the MTR. Estimated exposure is 3×10^{20} fissions/ cm^3 or 10,000 Mwd/ton of UO_2 - PuO_2 . It was decided not to recharge the high density UO_2 -4.13 mole % PuO_2 capsule (GEH-14-86)

because of the time delay to complete the required hot cell leak test. Both capsules were sent back to Hanford and radiometallurgical examination has started. Dimensional data on the as-received capsules is shown below:

DIMENSIONAL DATA

Exposure GEH-14 Number	0 Fissions/cm ³		1.6 x 10 ²⁰ fissions/cm ³		3.0 x 10 ²⁰ fissions/cm ³	
	Diameter, inch	Length, inch	Diameter, inch	Length, inch	Diameter, inch	Length, inch
85	0.575	2.467	0.578	2.465	0.592*	2.471
86	0.574	2.091	0.576	2.085		

* OD varies from 0.578 to 0.592 at middle of capsule

The capsules are presently being drilled for fission gas collections and analysis. A paper, HW-SA-2675, summarizing the work to date on the irradiation testing of all 24 UO₂-PuO₂ capsules in this set has been accepted for presentation at the American Nuclear Society Winter Meeting in November, 1962.

Instrumentation modifications to the VH-4 Hydraulic Rabbit Facility have not been completed. Authorization to proceed with this step was given in June. Irradiation of the four specimens (GEH-21, 13, 14, 15, and 16) containing UO₂-0.154 mole % PuO₂ and UO₂ (1.00 mole % U²³⁵) cannot begin until this work is done.

PRTR Prototype UO₂-PuO₂ Irradiation Testing - M. D. Freshley

The 42-inch long UO₂-PuO₂ cosine enriched seven-rod cluster is being examined in Radiometallurgy. The PuO₂ enrichment was varied along the length of this element to obtain longitudinal power flattening. It operated for 27 full power days in the ETR high temperature loop to a maximum exposure of 1100 Mwd/ton. Autoradiographs made from the irradiated fuel rods show areas of high fission product concentration due to plutonium segregation within loaded increments. Dark spots on the external surface

because of the time delay to complete the required hot cell leak test. Both capsules were sent back to Hanford and radiometallurgical examination has started. Dimensional data on the as-received capsules is shown below:

DIMENSIONAL DATA

Exposure GEH-14 Number	0 Fissions/cm ³		1.6 x 10 ²⁰ fissions/cm ³		3.0 x 10 ²⁰ fissions/cm ³	
	Diameter, inch	Length, inch	Diameter, inch	Length, inch	Diameter, inch	Length, inch
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86	0.574	2.091	0.576	2.085		

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FIGURE 3.2

Photomicrograph Showing a $\text{UO}_2\text{-PuO}_2$ Particle Bonded to the Zircaloy Cladding in the Region of a Hot Spot 250X

FIGURE 3.3

Transverse Cross Section Through Hot Spot in $\text{UO}_2\text{-PuO}_2$ Fuel Caused by Segregation 5X

FIGURE 3.4

Longitudinal Section of UO_2 - PuO_2 Core Through a Hot Spot Caused by PuO_2 Segregation and an Autoradiograph of the Polished Section 4X

The longitudinal sections taken through these areas (Figure 3.4) are interesting in that the columnar grain growth areas are not symmetrical, the void is not centrally located in the columnar grain growth region, the center void is elliptical and not circular, and the columnar grains in the radial direction are smaller than the columnar grains in the longitudinal direction. Also, these fuel rods were irradiated in the vertical position and the large voids which have formed are displaced

toward the top of the hot spots. There are lenticular shaped voids and spherical inclusions (tentatively identified as metallic uranium) in the columnar grain growth regions as shown in Figure 3.5. This structure is characteristic of irradiated UO_2 .

FIGURE 3.5

Columnar Grains, Lenticular Voids, and Spherical
Inclusions in Irradiated UO_2 - PuO_2 250X

Harder, high-porosity particles were observed in the irradiated UO_2 - PuO_2 fuel material as shown in Figure 3.6 and 3.7. These particles are thought to be PuO_2 or PuO_2 -rich solid solution. This indicates that some of the PuO_2 was in the form of larger sized particles (0.005-inch diameter) or that the small particle size PuO_2 enrichment has agglomerated. The appearance of the particles is different depending on the structure and hence the operating temperature of the surrounding material, i. e., the particles lose their identity by diffusing into the more dilute UO_2 - PuO_2 at the higher operating temperatures and no such particles are observed in the central regions of the hot spots.

FIGURE 3.6

Photomicrograph Near the Edge of an Irradiated $\text{UO}_2\text{-PuO}_2$ Swaged Fuel Core Shows a High-Porosity Plutonium-Rich Particle Surrounded by Unsintered $\text{UO}_2\text{-PuO}_2$ Fuel 250X

FIGURE 3.7

Photomicrograph of a Region in a Swaged $\text{UO}_2\text{-PuO}_2$ Fuel Rod Which Has Undergone In-Pile Sintering (A particle of high concentration which has not diffused into the more dilute $\text{UO}_2\text{-PuO}_2$ is shown.) 250X

Autoradiographs made from the polished cross sections as shown in Figure 3.4 show that no discernable fission product migration has occurred in those areas which have experienced equiaxed grain growth. Some localized fission product migration is evident however, in those regions where central void formation and columnar grain growth has occurred. The autoradiographic technique being used has poor resolution and a more precise analytical method might show some migration under both conditions.

MgO-PuO₂ and ZrO₂-PuO₂ Irradiation Capsules - M. D. Freshley
and D. F. Carroll

Eight Zircaloy-clad capsules (1/2-inch diameter x 4 inches long) containing MgO-PuO₂ fuel pellets and eight containing ZrO₂-PuO₂ fuel pellets have completed their irradiation in the ETR. MgO - 3.09 wt % PuO₂ and MgO - 13.52 wt % PuO₂ pellets as well as ZrO₂ - 2.18 wt % PuO₂ and ZrO₂ - 10.39 wt % PuO₂ pellets were irradiated at different core temperatures for different periods of time. Estimated maximum core temperatures for the MgO-PuO₂ specimens were 1700 and 2200 C and estimated maximum temperatures for the ZrO₂-PuO₂ samples were 1600 and 2800 C.

Four of the irradiated MgO-PuO₂ samples are being examined. Transverse cross sections of the samples show that general cracking has occurred in the specimens which operated at the lower power generations as shown in Figure 3.8. Center voids and columnar grains have formed in the MgO-PuO₂ samples which operated at the higher power generations as shown in Figure 3.9. Because of its better thermal conductivity and smaller radial thermal gradients, the MgO-PuO₂ sintered pellet fuel material has fewer cracks than is characteristic of irradiated UO₂.

A cursory examination of the ZrO₂-PuO₂ specimens showed that discolored areas indicative of hot spots are present on the external surface of some of the samples. The Zircaloy cladding on one of the capsules containing ZrO₂ - 10.39 wt % PuO₂ pellets which operated at a power generation of about 22 kw/ft ($\int kd\theta = 58$ w/cm) has failed even though there were

MgO - 3.09 wt % PuO₂ Irradiated to 6.36×10^{20} nvt at a Power
Generation of 29 kw/ft ($\int kd\theta = 77$ w/cm) 4X

FIGURE 3.8

MgO - 13.5 wt % PuO₂ Irradiated to 1.1×10^{20} nvt at a Power
Generation of 19.2 kw/ft ($\int kd\theta = 51$ w/cm) 4X

MgO - 3.09 wt % PuO₂ Irradiated to 8.02×10^{20} nvt at a Power
Generation of 36 kw/ft ($\int kd\theta = 95$ w/cm) 4X

FIGURE 3.9

MgO - 13.5 wt % PuO₂ Irradiated to 2.17×10^{20} nvt at a Power
Generation of 37.6 kw/ft ($\int kd\theta = 100$ w/cm) 4X

no rupture indications during operation in the ETR. The ruptured capsule is shown in Figure 3.10. Two longitudinal cracks about 1/2-inch long and 1/4-inch apart have opened up at one end of the capsule. The cladding has not swelled appreciably suggesting a brittle type failure. Further examination of the capsule is being made to determine the cause of failure.

FIGURE 3.10

Zircaloy-Clad ZrO_2 - 10.39 wt % PuO_2 Capsule Which Failed During
Irradiation in the ETR. Power generation about 22 kw/ft
($\int k d\theta = 58$ w/cm) with a maximum core temperature of about 2750 C
1-1/3X

Neg. No. B-1918

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MgO-PuO₂ Test Element For PRTR Irradiation - M. D. Freshley,
R. E. Bardsley and R. E. Sharp

A full size Zircaloy-clad 19-rod cluster element containing MgO-PuO₂ fuel material was fabricated by swage compaction for irradiation testing in the PRTR. This type of element is of interest as a high temperature plutonium containing ceramic spike fuel.

Process tube activity records indicate that the element failed in the PRTR after about 3 hours of 60 Mw operation and the element was discharged after an exposure of about 8 Mwd due to excessive coolant activity. During this time, it was subjected to several thermal cycles.

A cladding rupture was observed on one of the fuel rods in the element during examination in the fuel discharge pit and the rod was removed from the cluster and sent to Radiometallurgy for a more detailed examination to determine the cause of failure. A longitudinal split occurred on the outside rods in the cluster about 36 inches from the top of the element. The split is about 1-1/2 inches long and has opened up about 1/4 inch at the widest point as shown in Figure 3.11. Measurements indicate that about 2 inches of fuel are missing below the failure point (upstream end) and about 6 inches of fuel has washed out above the split in the cladding, (downstream end). A total of about 9.5 inches of core material containing about 1.8 grams of plutonium has washed out of the fuel rod. The maximum calculated core temperature for this fuel element operating in the PRTR was about 900 C and no appreciable in-reactor sintering was expected to occur under these conditions. This unsintered type core material is susceptible to water-logging if water penetrates the cladding. The cladding has swelled in the immediate region of the failure. This swelling and the ductile type failure suggests an internal pressure probably from steam pressure as a result of water logging and/or from the volume increase of MgO as a result of hydration. Rod diameter measurements taken on each side of the failure were unchanged except for a localized diameter increase which occurred about 2 inches below the failure (an increase of 0.036-inch) and one which occurred

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3.16

HW-74718

FIGURE 3.11
Ruptured Rod From 19-Rod Cluster MgO-PuO₂ Element

RM-15494
AEC-GE RICHLAND, WASH.

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about 6 inches above the failure (an increase of 0.013 inch). A longitudinal cross section of one of these swelled areas is shown in Figure 3.12. It shows that the core corrosion has proceeded to this point and some hydration of the MgO has occurred.

FIGURE 3.12

Longitudinal Cross Section Taken Through an Area of Localized Swelling on the Failed MgO-PuO₂ Fuel Rod

Autoradiographs made by exposing the ruptured rod to glass show areas of high fission product concentration caused by plutonium segregation in the fuel material. It is possible that such an area of abnormally high heat generation might have contributed to the cause of failure; however, there are no indications of cladding burnout or any signs of nonuniform discoloration of the cladding surface.

The cladding in the immediate region of the rupture is being examined metallographically. Results of this examination at one end of the split indicate that there were no cladding defects such as long internal cracks; there is no observable reaction between the MgO-PuO₂ core and the Zircaloy cladding; the zirconium hydride concentration is about normal for autoclave tested zirconium; the fracture was ductile; and the cladding structure in some areas is characteristic of a strained material.

Neg. No. B-2053

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ICARUS, HELIOS, and ARGUS Experiments - W. J. Bailey and
S. H. Woodcock

No work was done on the ICARUS experiment this period.

The bellows assembled for the HELIOS Experiment were received from the vendor. Possible delivery data for the modified thermocouple is still uncertain though the vendor representative was here in September to verify allowable welding methods at two of the thermocouple sheath junctions.

No work was done on the ARGUS Experiment other than to continue the graphical layout of the apparatus.

Injection-Cast Capsule - W. J. Bailey and R. K. Koler

Radiometallurgical examination of the irradiated Zircaloy-clad capsule (GEH-14-27) containing an Al - 2.1 wt % Pu - 2.0 wt % Ni alloy core and fabricated by injection casting has been completed. Photographs of the capsule may be seen in Figures 3.13 and 3.14. In Figure 3.14 the black areas within the core material are not voids in most cases and under proper conditions disclose a distinct grain structure. No evidence of hydriding was observed in the Zircaloy-2 cladding. The presence of a second phase in the core may be clearly noted in Figure 3.14. The darker portions of the discolored surface are believed to be associated with areas in which the initial brittle core-clad metallurgical bond has fractured. This specimen (9/16-inch OD by 3.6 inch) maintained a specific power of about 25 kw/ft (shifted periodically to a higher neutron flux zone). It had an exposure of 83×10^{18} fissions/cm³ and a plutonium burnup of 60%.

FIGURE 3.13

Irradiated Zircaloy-Clad Capsule (GEH-14-27) with Al-2.1 wt % Pu-2.0 wt % Ni Alloy Fuel Core Fabricated by Injection-Casting (Irradiation history: specific power-25 kw/ft, exposure- 3×10^{20} fissions/cm³, and plutonium burnup-60%. Dark areas are believed to be regions where core-clad bond has fractured.) 1X

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(a) A-9896 75X

(b) 9887 250X

(c) A-9547 250X

(d) A-9549 250X

FIGURE 3. 14

Irradiated Injection-Cast Capsule (GEH-14-27)

(The center of the Al-2.1 wt % Pu-2.0 wt % Ni alloy core is shown in (a) and (b) intact and fractured core-clad bonds are shown in (c) and (d) with the Zircaloy-2 cladding located at the right.)

Plutonium Ceramics ResearchPlutonium Oxide - R. E. Skavdahl

As part of a program aimed at the construction of a Pu-O phase diagram, several quenching and annealing studies were performed.

Cooling a sample of α -Pu₂O₃ (PuO_{1.62}) at 10 to 15 C per minute from 1000 C in a helium atmosphere yielded a mixture of approximately 80% FCC α -Pu₂O₃ and 20% BCC α -Pu₂O₃. Cooling a sample of α -Pu₂O₃ to room temperature in a vacuum of 1×10^{-6} mmHg from 600 C at 65 C per hour gave a two-phase mixture of PuO₂ and what appeared to be PuO.

Another sample of α -Pu₂O₃, which oxidized to PuO_{1.77} at some time during the experiment, was quenched from 900 C and yielded a single phase fluorite structure with $a_o = 5.404 \pm 0.001A$. This is in excellent agreement with the lattice constant predicted on the basis of a linear lattice spacing composition plot between PuO₂ ($a_o = 5.396A$) and α' -Pu₂O₃ ($a_o = 5.409A$).

Several samples with $\frac{O}{Pu}$ ratios of 1.77, 1.80, 1.85, and 1.86 were heated to 600 C, held there for several days, and then cooled to room temperature at a rate of 7.8 C per hour. Resultant X-ray powder pattern analyses showed, for each sample, a two-phase mixture of body centered cubic α -Pu₂O₃ with $a_o = 11.04 \pm 0.01A$, and face centered cubic PuO₂ with $a_o = 5.397 \pm 0.001A$. The latter phase may be slightly oxygen-deficient to the extent of approximately PuO_{1.98}, which would explain its slightly higher value of lattice constant.

Melting studies showed α -Pu₂O₃ to melt congruently at 2360 ± 30 C and β -Pu₂O₃ to melt congruently at 2085 ± 25 C.

PuO₂ Compatibility Tests - R. E. Skavdahl

Samples of 50 mole % PuO₂ powder and 50 mole % metal powder were mixed and pressed into pellets for compatibility studies. After firing at 1700 C for 2 hours in a helium atmosphere, X-ray powder pattern analyses and photomicrographs showed very little reaction for the PuO₂-molybdenum pellet, some observable reaction for the PuO₂-tungsten pellet, and

apparently considerable reaction for the PuO_2 -tantalum pellet. The powder pattern for the PuO_2 -tantalum mixture revealed no observable tantalum lines after firing.

PuO_2 -Carbon Reactions - R. E. Skavdahl

Mixtures of PuO_2 powder and graphite powder were pressed into pellets for subsequent firing in an attempt to prepare samples of $\beta\text{-Pu}_2\text{O}_3$, PuO , and PuC . The samples are listed below:

<u>Sample</u>	<u>PuO_2 gram</u>	<u>Carbon gram</u>	<u>Desired Product</u>
1-18	9.9988	0.2220	$\beta\text{-Pu}_2\text{O}_3$ ($\text{PuO}_{1.50}$)
1-19	9.9995	0.4440	PuO
1-20	9.9986	1.3300	PuC

After firing in a helium atmosphere at 1800 ± 50 C for 5-1/2 hours, X-ray powder patterns revealed:

For sample 1-18, only lines for $\beta\text{-Pu}_2\text{O}_3$ were observed. A second, more finely grained film was run and again showed only $\beta\text{-Pu}_2\text{O}_3$. The sample was observed to melt congruently at 2085 ± 25 C.

For sample 1-19, a major cubic phase with a lattice parameter of $4.962 \pm 0.001\text{\AA}$ was observed as well as a minor phase of $\beta\text{-Pu}_2\text{O}_3$ and possibly a very slight amount of a third phase. The major cubic phase parameter of $4.962 \pm 0.001\text{\AA}$ agrees very well with that of $4.96 \pm 0.01\text{\AA}$ reported for PuO by Ellinger. ⁽¹⁾

For sample 1-20, a major cubic phase (approximately 95%) with lattice parameter of $4.9710 \pm 0.0005\text{\AA}$ and a second minor phase (approximately 5%) were observed. The major phase indexed well as PuC and the minor phase indexed well as Pu_2C_3 .

In a further attempt to purify and/or transform to single-phase, a sample of 1-19 was heated in vacuum at 900 C for 8-1/2 hours and then quenched in liquid nitrogen. (This was labeled sample 1-35.) X-ray

powder pattern analysis showed again a major cubic phase ($a_0 = 4.961 \pm 0.001\text{\AA}$), a minor phase of $\beta\text{-Pu}_2\text{O}_3$, and possibly a very small amount of a third phase.

Carbon analyses were performed on all four samples with the following results:

<u>Sample</u>	<u>Wt % Carbon</u>
1-18	Undetectable
1-19	0.180
1-20	4.83
1-35	0.083

The conclusion reached as a result of these experiments is that $\beta\text{-Pu}_2\text{O}_3$, PuO, and PuC can be synthesized by the reaction between PuO₂ and carbon. The degree of purity obtainable by this method, however, is still a matter for further investigation. In the case of sample 1-20, the mixture of PuC and Pu₂C₃ rather than single-phase PuC is to be expected, since the stoichiometry was such that at completion of reaction, there would be 50 at. % carbon. Single-phase PuC exists only in the region of about 45 to 47 at. % and therefore would not be expected to be produced in sample 1-20.

Emf Measurements - C. E. McNeilly

Electrical resistivity and thermal emf measurements have been carried out on plutonium dioxide, suboxides and plutonium carbide.

PuO_{2.00} displays a continuous resistivity versus $\frac{1}{T}$ curve with an activation energy of 1.8 ev. Room temperature resistivity was about 10^{10} ohm-cm, however because of impurities, there was a transition from extrinsic to intrinsic conductivity in the region of room temperature. Extrapolated from the high temperature portion, the resistivity at 30 C would be 10^{14} ohm-cm.

Measurements on $\text{PuO}_{1.72}$, $\text{PuO}_{1.84}$, $\text{PuO}_{1.92}$ and $\text{PuO}_{1.96}$ all showed discontinuities indicative of phase transformations. The activation energies and resistivities are tabulated below.

O/Pu	ρ 298 K	$\Delta E (< T_t)$	T_t (K)	$\Delta E (> T_t)$
1.72	8×10^4	0.95	760	0.54
1.84	2×10^6	1.11	920	0.49
1.92	$1.5 \times 10^{7*}$	1.23	900	0.52
1.96	$1 \times 10^{8*}$	1.28	850	0.51

* Extrapolated

$\text{PuO}_{1.72}$ has a resistivity at 1000 C only about 0.05 ohm-cm.

The constant ΔE for all samples above the transformation temperature are indicative of a single-phase, whereas the change in ΔE with composition at low temperatures arises from the presence of two-phases— $\text{PuO}_{1.62}$ and $\text{PuO}_{1.98}$.

Thermal emf measurements have shown that PuO_{2-x} normally exhibits p-type conductivity, due to the $\text{PuO}_{1.62}$ which is an oxygen excess Pu_2O_3 . Above the transformation temperature it is anticipated that n-type conductivity, due to oxygen-deficient PuO_2 phase, should appear. Measurements are currently under way to confirm this.

Measurements on some composition in the neighborhood of $\text{PuO}_{1.97}$ and $\text{PuO}_{1.99}$ have shown n-type conductivity at room temperature, indicating single-phase oxygen-deficient PuO_2 .

Resistivity studies on PuC have been limited to compositions in the neighborhood of 37 and 39 at. % carbon. Both of these are two-phase compositions consisting of alpha-plutonium and PuC_{1-x} . The 37 at. % sample has a resistivity of 248μ ohm-cm while the 39 at. % sample is 297μ ohm-cm. Both of these are remarkably constant with temperature; staying within $\pm 3\%$ up to 600 C. (Limit of accuracy of meter.)

Plutonium Carbides - J. B. Burnham and T. D. Chikalla

The as-cast carbide series ranging from 12 to 52 at. % C have been given three different heat treatments. In the first case the samples were held for 124 hours at 600 C and then cooled to room temperature at 100 C per hour. In the second case they were held at 600 C for 168 hours and cooled at 7.8 C per hour. The third heat treatment consisted of a quench from 600 C into liquid nitrogen.

Micrographic examination of the slowly cooled samples showed a considerable change over the as-cast structure. In the as-cast condition there was little if any evidence of the zeta (Pu_3C_2) phase. When the samples were slowly cooled from 600 C, though, those below 41 at. % C showed the characteristic bladelike structure associated with the zeta phase. The progressive growth of this phase is shown in Figure 3.15, 3.16 and 3.17. In the as-cast micrograph (Figure 3.15) primary dendrites of PuC are visible in a matrix of PuC. The incipient zeta phase can be seen in the form of small blades. In Figure 3.16 the effect of cooling rate on zeta formation can be clearly seen. Microhardness measurements of a number of blades and grains in this particular sample indicated that the massive grains are PuC almost completely transformed to zeta. Whereas PuC has a microhardness of 600 to 700 DPH, these areas both were in the 165 to 185 DPH range. The more slowly cooled sample of Figure 3.17 shows even more complete transformation to zeta and growth of the blades.

It should be noted that the zeta phase is not always detected on cast samples. In one case a 39.9 at. % C sample was remelted as a 5 gram button. Whereas the slowly cooled, large sample had shown definite metallographic and X-ray evidence of zeta, the small remelted button showed none.

X-ray diffraction analysis of the series had shown the same type of variation in the PuC defect lattice as previously noted in very small samples. In the as-cast condition the value for the lattice constant varied from $4.9738 \pm 0.0006\text{\AA}$ for carbon-rich PuC to $4.950 \pm 0.003\text{\AA}$ for carbon-poor PuC. The

FIGURE 3.15

As-Cast 26.0 at. % Alloy Primary Dendrites of PuC in a Matrix of Alpha-Plutonium. (A few blades of zeta can be seen) 250X

FIGURE 3.16

Composition 26.0 at. % C. Heated 124 Hours at 600 C, and Cooled at 100 C Per Hour. Blades of Zeta Visible in Matrix of Alpha-Plutonium 250X

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FIGURE 3.17

Composition 26.0 at. % C. Heated 168 Hours at 600 C, and Cooled at 7.8 C Per Hour. Large Zeta Blades in Alpha Plutonium Matrix 250X

carbon-rich value agrees remarkably well with that of Mulford et al. who report 4.9737A. After the lattice parameter goes through the minimum value at about 38 at. % C, it rises to a constant value of 4.958A which corresponds to the Mulford value for carbon-poor PuC.

The reason for this minimum point on the a_0 versus carbon curve has not as yet been explained. The slowly cooled samples showed little difference in lattice parameter as a function of cooling rate. In comparison to the as-cast parameters of the same composition the slowly cooled pieces all showed an increase in lattice parameter. Instead of showing a minimum below 37 at. % C they yield a minimum value of 4.964A at approximately 45 at. % C. The maximum value of $4.9768 \pm 0.0006A$ is reached at slightly less than 49 at. % C. Figure 3.18 illustrates these variations. As mentioned above, the values for analyses below 41 at. % C are scattered since the high angle X-ray lines are very diffuse. It is even possible that the lattice parameters for samples below 41 at. % C

in actuality are calculated from zeta lines or are strongly influenced by these lines since there is considerable overlap of the two patterns.

PuC LATTICE PARAMETER vs CARBON CONTENT

FIGURE 3. 18

Plot of PuC Lattice Parameters as a Function of Carbon Content and Heat Treatment. Some values for data error are shown. The effects of the line broadening in samples below 41 at. % C are reflected in the large error terms for these points.

In the samples quenched from 600 C into liquid nitrogen the lattice parameter below 41 at. % C is independent of carbon content. As can be seen in Figure 3.18 the value stays essentially constant at 4.954Å. The X-ray patterns of these quenched samples were all sharp and strong. This implies that the zeta peritectoid is, indeed, below 600 C and that the reaction kinetics are such that it is possible to quench through this region

fast enough to inhibit the reaction. This confirms the data which was gathered from the as-cast samples where evidence of the zeta phase was often detected only in the broadening of the PuC X-ray lines.

The reason for failure to see the formation of zeta in samples of 41 at. % C slowly cooled from 600 C is not clear. Figure 3.19 shows the abundance of zeta blades in a slow cooled 39.9 at. % C rod. In Figure 3.20, a 41.0 at. % alloy, there can be found little or no evidence of the zeta phase. There is, though, a grain boundary phase which appears to be alpha-plutonium. Further heat treatments in the 40 at. % C region are being run to try to explain this anomaly.

FIGURE 3.19

Zeta Blades in a Matrix of Alpha-Plutonium
39.9 at. % C Sample Cooled at 7.8 C Per Hour From 600 C 250X

FIGURE 3.20

Primary Grains of PuC With Alpha-Plutonium at the
Boundaries in a Slowly Cooled 41.0 at. % C Rod 250X

Plutonium Nitride - D. F. Carroll

A high temperature-high vacuum horizontal X-ray diffractometer attachment was used to obtain lattice expansion data in the temperature range 26 to 800 C. Measurements at higher temperatures were prevented by oxidation of the PuN at 1×10^4 mmHg, air. The linear equation which best fits the lattice data was determined by the method of least squares. The average coefficient of linear thermal expansion calculated from this equation is $13.80 \times 10^6 / \text{C}$. The plutonium mononitride used for these experiments was prepared by reacting -325 mesh plutonium hydride with gettered nitrogen at 600 C. The product is single-phase PuN by X-ray diffractometer analysis.

Microhardness data were obtained on dendritic PuN formed by arc-melting plutonium under one atmosphere of nitrogen. The surface of the specimen was electropolished in a tetraphosphoric acid solution prior to testing. A Vickers 136 degree diamond pyramid indenter was used with a 200 gram load. Photomicrographs show cracking at each indentation, thus clearly displaying the brittle nature of PuN. See Figure 3. 21, negative number 8064. The average diamond pyramid hardness number, DPH, computed from the best indentations is 370 kg mm^{-2} .

FIGURE 3. 21

Microhardness Indents in PuN Dendrites
(Note cracking)
500X

Neg. No. 8064

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Plutonium Sulfides - Y. B. Katayama

A sample of plutonium hydride was reacted with one atmosphere of hydrogen sulfide at 540 C for 24 hours. The resultant product was a black appearing powder with a four-fold increase in bulk volume.

X-ray diffraction of a powder sample showed the product to be Pu_2S_3 coexisting with a weak unidentified phase. The remaining powder was then readily compacted into a pellet and arc-melted under argon. This process reduced the quantity of unidentified phase. The arc-melted button had a metallic lustre upon chilling on the copper hearth.

The lattice constant by extrapolation of a plot of "a" versus $1/2 \left(\frac{C_{os}^2 \theta}{\sin \theta} + \frac{C_{os}^2 \theta}{\theta} \right)$ was found to be 8.423 for this body centered cubic structure.

Special Plutonium Fuel Fabrication for Other DRD ProgramsPlutonium-Aluminum Alloy Fuel for the Light Water Critical Experiment - C. H. Bloomster and L. C. Lemon

High exposure plutonium-aluminum alloy, Zircaloy-clad fuel rods are being fabricated for the light water critical experiment to be conducted by Physics and Instrument Research. One thousand 4-foot long rods made with 17 wt % Pu^{240} are required. One hundred ten Al-2 wt % Pu billets have been cast for extrusion into rod. This is enough material for approximately half the rods.

Fission Product Transient Samples for Phillips - W. T. Ross, L. C. Lemon and C. H. Bloomster

Seventy-two fission product transient samples for Phillips Petroleum Company are currently being fabricated. As previously reported, these aluminum coextrusion-clad, tubular elements have a nominal 0.80-inch OD, and 0.060-inch wall, and are 4 inches long. The inner and outer cladding and

core are 0.020-inch thick. The core length is 3 inches. The cores consist of 18 aluminum base alloys plus plutonium, U^{235} , U^{233} , and lithium of varying compositions.

Casting of the core alloys is done in an electrical resistance furnace using graphite crucibles and molds. Core rings are machined to size and weight, chemically cleaned, and assembled into billets. (Figure 3.22) Three cores are assembled in tandem with aluminum rings as spacers.

FIGURE 3.22

Assembled and Unassembled Coextrusion Billets
Dark rings simulate core alloys separated with aluminum spacers.

The billets are hot outgassed and extruded at a 10 to 1 reduction in area, over a floating mandrel, using a streamlined die with a 60 degree entrance angle. (Figure 3.23) Following extrusion, the tubes are radio-graphed for core location and machined to length. Prior to final assembly, each sample is ultrasonic bond tested, autoclaved, and visually inspected.

FIGURE 3. 23

Floating Mandrel and Extrusion Die, Assembled Billet,
Coextruded Tube, Finished Capsule

The end caps and thermocouple tubes are then held in place with a fixture. Welding of the end caps is done in a glass lathe using a tungsten inert gas process with alternating current. A single burn down pass is made for each end cap without use of filler metal. (Figure 3. 24) Two final radiographs are taken at 90 degree angles for checking core location and measuring wall thickness. (Figure 3. 25)

Sixteen of the completed capsules containing aluminum-plutonium alloy cores have been completed and shipped. Twenty-four aluminum-U²³⁵ bearing capsules are currently in the final assembly step. The remaining pieces are being fabricated when satisfactory analytical results are obtained.

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FIGURE 3.24

Below: Fuel Tube, End Caps, Thermocouple Tubes
Above: Finished Capsule

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FIGURE 3.25

Final Radiographs of Two Capsules Taken at Right Angles
(This photograph does not show outer cladding thickness)

PuC and Pu₂C₃ Standards - J. B. Burnham

Pure PuC and Pu₂C₃ standards have been prepared by arc-melting for use with a microprobe analyser. The PuC button had a carbon content of 46.7 at. % C and the Pu₂C₃ showed 62.0 at. % C. The latter sample was rather difficult to make since a considerable amount of carbon was lost in the arc. An excess was added to compensate for the loss, but the actual depletion proved to be less than anticipated. X-ray examination of these specimens show them to be single-phase PuC and Pu₂C₃ respectively.

Classification of PuO₂ - J. B. Burnham

Approximately 3.5 grams of high exposure (30% Pu²⁴⁰) PuO₂ was classified into five size ranges for Biology Operation for inhalation studies. The size ranges were as follows:

1. Greater than 5 μ
2. 1 to 5 μ
3. 0.5 to 1 μ
4. 0.1 to 0.5 μ
5. Less than 0.1 μ

The PuO₂ was calcined in air for 2 hours at 900 C. After calcining it was ground in a new mortar and pestle. The classification was accomplished by settling in water to which a deflocculent had been added. The effect of the high temperature calcining was to increase the mean particle diameter to an estimated 10 μ . This is compared with the value of 2 μ previously found for material of the same type which had been calcined at 300 C and not ground.

REFERENCES

1. Ellinger, F. H. "A Preview Of The Intermetallic Compounds Of Plutonium," The Metal Plutonium. 281-308. The University of Chicago Press, 1961.

4.0 SPECIAL FABRICATION OF PLUTONIUM AND OTHER RADIOACTIVE MATERIALS

Heat Capacity of Plutonium Carbide - P. G. Pallmer

Direct determination of the heat capacity of plutonium carbide has been attempted experimentally. Indirect determinations are available but published direct measurements are not known. The calculated heat capacity⁽¹⁾ to 1000 C varies from 13 to 16 cal/g-mole°.

Four 1-inch disks of plutonium monocarbide containing some plutonium sesquicarbide were used for capacity determination. The vacuum glove box housing the rolling mill provided a nitrogen atmosphere which was to prevent oxidation. However, the temperature was limited to 350 C because of oxidation at higher temperatures. At 350 C the edges of the disk had a tendency to crumble.

The sample disk was manipulated by holding it between stainless plates welded to crucible tongs. The temperature was recorded with a thermocouple in a similar stainless disk welded in place as shown in Figure 4.1. Fiberfrax insulation was added to minimize the temperature drop during transfer. The thermocouple was calibrated against the freezing point of tin.

The hot disk was placed between copper blocks to measure the heat content by the temperature rise. Typical curves are shown in Figure 4.2. A quadruple thermopile was arranged as shown in Figure 4.1.

A 1-inch silver disk was used as a reference standard to estimate the heat loss in manipulating the hot disk. The loss amounted to about 7% of the heat content of the larger carbide disks, as tabulated in Table 4.1. This correction was believed to come mostly from loss during transfer, therefore, an additive correction rather than the more conventional ratio was used.

From a temperature of 350 to 30 C the heat capacity was measured as 10.7 ± 0.6 cal/g mole° as compared to the calculated C_p^{450} of 13.34. This

FIGURE 4.1

Tongs for Holding Sample and Thermocouple in Furnace

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discrepancy is some four times either the heat loss correction or the deviation in measured values. The precision did not warrant any more refined treatment of the data than described here, including the simple extrapolation shown in Figure 4.2. Greater accuracy would require more elaborate apparatus of the drop type.

FIGURE 4.2
Calorimeter Heating Curves
(Temperature rise of 1855 gram copper)

TABLE 4.1

PLUTONIUM CARBIDE HEAT CAPACITY MEASUREMENTS

Reference	Wt/gram	$\frac{\Delta T}{C}$	Measured C cal/g°	Heat Loss* cal/g°
Silver	16.725	309	0.0496	0.14
		324	0.0508	0.12
		332	0.0529	0.11
		317	0.0489	0.15
		328	0.0512	0.11
		328	0.0529	0.09
				0.12 Average

Sample Number	Wt/gram	$\frac{\Delta T}{C}$	Measured C_p cal/g $^\circ$	Heat Loss cal/g $^\circ$	Corrected C_p cal/g $^\circ$	$C_p^{PuC \pm 251}$ cal/g-mole $^\circ$
45	22.2	347	0.0354	0.0053	0.0406	10.2
		332	0.0381		0.0434	10.9
		343	0.0396		0.0448	11.2
		332	0.0390		0.0443	11.1
81	41.0	300	0.0396	0.0028	0.0424	10.6
		330	0.0393		0.0421	10.6
		302	0.0400		0.428	10.7
75	40.0	334	0.0412	0.0029	0.0441	11.1
		338	0.0394		0.0423	10.6
		350	0.0390		0.0419	10.5
74	42.7	341	0.0397	0.0027	0.0424	10.6
		323	0.0396		0.0423	10.6
		334	0.0410		0.0437	11.0
						10.7 $\pm$ 0.6

* From heat capacity of silver as given in J. Am. Chem. Soc. 46: 1178. 1924. 0.0580 Cal/g° at 180 C.

REFERENCES

1. Krikorian, O. H. Estimation of High-Temperature Heat Capacities of Carbides. UCRL-6785. February 6, 1962.

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