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THE PREPARATION OF FLUTONIUM POWDER BY A HYDRIDING
PROCESS--INITIAL STUDIES

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THE PREPARATION OF PLUTONIUM POWDER BY A HYDRIDING PROCESS--
INITIAL STUDIES

I. INTRODUCTION

Powder metallurgy is rapidly gaining importance as a means of fabricating nuclear fuel elements and other reactor components. It provides a convenient method for forming metals, unusual combinations of metals, and metal-ceramic combinations. The unique features of this technique which make it desirable for nuclear engineering purposes are the following:

1. Metal and ceramic combinations (cermets), which are being used more and more in the production of dispersion-type fuel elements, cannot be fabricated by more conventional methods.
2. Powder metallurgy methods produce a material which contains a large number of uniformly distributed crystal-lattice defects. This type of material changes less under irradiating conditions than materials with ordered crystal lattices.
3. Powder metallurgy processes take place at temperatures below the melting point of the material being used. The tremendous difference in melting temperature between plutonium and molybdenum or zirconium makes it impossible to alloy these metals by conventional methods. They can only be alloyed by means of powder metallurgy.

Plutonium powder, like uranium powder,⁽⁴⁾⁽⁵⁾ can be prepared from massive metal by a hydriding process. This process involves the conversion of metal into hydride, and then the decomposition of hydride back to metal.

This paper investigates the possibility of preparing plutonium powder from massive metal by the hydride process. Factors which affect initiation of the hydriding reaction and particle size of the metal powder are discussed. An apparatus and procedure for powder production on a 500-gram scale are proposed.

II. SUMMARY AND CONCLUSIONS

Micron-sized plutonium powder was produced, in 20-gram batches, by hydriding massive metal and then grinding and decomposing the hydride.

Plutonium hydride was prepared in the following manner:

An apparatus containing clean plutonium metal was evacuated to a pressure of 10 microns. The vacuum was valved off, and dry oxygen-free hydrogen was introduced into the apparatus. The apparatus was then placed in a furnace and heated until the hydrogen and metal began to react. As soon as the reaction started, the apparatus was removed from the furnace. Hydrogen was fed into the apparatus until all of the metal was converted to hydride. The

hydride was then decomposed by heating it to 400 C in the apparatus at a vacuum of three microns.

The hydriding reaction could only be initiated between dry, oxygen-free hydrogen and clean metal.

Heat liberated by the reaction sintered the hydride powder into a granular frit. The size of these grains (up to 1/8 inch) was nearly independent of the size and shape of the starting metal or the reaction rate.

Metal produced by decomposing its hydride was porous and would not subdivide further during additional hydriding cycles.

Sintering effects made it necessary to agitate the powder during the dehydriding step. Sintering appeared to begin at about 300 C. A loose sinter cake was formed by 450 C. Beads of metal appeared in the sinter at about 600 C.

An apparatus was proposed for the production of plutonium powder on a 500-gram scale.

III. APPARATUS AND PROCEDURE

The apparatus used to prepare plutonium powder on an experimental, 20-gram scale is illustrated diagrammatically in Figure 1. Figure 2 is a diagram of the inert atmosphere glove box system which housed the apparatus.

Although variations were made in the hydriding process, the following is typical and will serve to illustrate the experimental apparatus and procedure.

Clean plutonium metal was loaded into a one-inch Vycor combustion tube, "A", through a removable end plate. The loaded combustion tube was out-gassed to a pressure of 10 microns by an oil diffusion pump, "P", through vacuum line "Z". It was then valved off from the vacuum line and connected to a bottle of hydrogen. Oxygen and water were removed from the hydrogen with a "Deoxyo" palladium catalyst, "H", followed by a "Drierite" drying column "J". The hydrogen-filled tube was inserted into an electric furnace, "B", and heated until the reaction began. As soon as the reaction was initiated, the tube was removed from the furnace. The rate of hydrogen consumption was measured with a rotameter, "X", in the hydrogen supply line. Temperatures were measured with a chromel-alumel thermocouple contained in a stainless steel thermowell, "O". The hydride was decomposed by heating it to 400 C in the tube at a vacuum of three microns. The metal powder was shaken from the tube into a vial, "I". The vial was then sealed off and removed.

During some runs, the frit or powder was mechanically agitated. A 60-cycle vibrator, "Y", which was attached to the combustion tube via

clamps and a ring stand, kept the individual particles in constant motion.

Powder size was determined by direct measurement. It was imbedded in polyester resin and photographed with a metallographic camera. These photographs were compared with photographs of a standard grid to determine particle size. Agglomeration by sintering during decomposition was determined from photographs taken before and after the decomposition process.

Size distribution of the frit was determined by screening a 200-gram sample of lightly-oxidized hydride.

The presence of hydride in the metal was detected by dropping some of the powder into a vial of water, and heating the water to 90 C. The amount of gas evolved was proportional to the amount of hydride.

IV. DISCUSSION

A. Principle Of The Hydride Process

The conversion of massive plutonium into powder by the hydride process occurs during the hydriding reaction due to the large density difference between the hydride (10.40 g/cc) and the metal (19.82 g/cc in the alpha phase).

Size reduction of the massive metal occurs only during the hydriding reaction; size and shape of the individual particles remained constant during the dehydriding step. Consequently, emphasis was placed on minimizing particle size of the hydride.

B. The Preparation Of Plutonium Hydride

The reaction between plutonium metal and hydrogen can be initiated and brought to completion only if the hydrogen is completely dry and oxygen-free. Ordinary bottled hydrogen contains water and oxygen in sufficient amounts to completely inhibit the hydriding reaction.

Surface purity of the metal also influenced initiation of the reaction. To assure prompt initiation, thick, loosely-adhering oxide was removed from the surface of the metal.

Plutonium hydride was readily prepared from the metal by the following method:

1. The apparatus (containing metal) was evacuated to a pressure of ten microns.
2. Dry, oxygen-free hydrogen was introduced into the apparatus.
3. The metal was heated in a hydrogen atmosphere until the hydriding reaction began.

4. The apparatus was removed from the furnace, while the metal and hydrogen reacted.

The hydriding reaction usually began at a temperature of about 50 C, or after about five minutes of heating. At that time, the metal began to take up hydrogen. A layer of fine, black powder (hydride) formed on the surface of the metal. Then, small particles of hydride began to flake away from the lump of metal. The lump swelled and grew larger. Finally, about fifteen minutes after the reaction began, the lump disintegrated into small pieces of grey, metallic-looking plutonium hydride. Particle size ranged from micron-sized powder to 1/8 inch granular frit. Lumps at various stages of the hydriding process are shown in Figure 3. A size distribution of the hydride frit is presented in Table I. The frit was brittle and could easily be broken up into a powder.

Prompt initiation of the hydriding reaction always involved heating the metal. Plutonium metal has a larger coefficient of thermal expansion than its oxide. Apparently, breaks occur in the oxide film when the metal is heated. Hydrogen reacts with the metal at these breaks to start the reaction. Plutonium has a much greater affinity for oxygen than hydrogen. As a result, any oxygen in the hydrogen repairs these breaks and stops the reaction.

Particle size of the hydride was primarily a function of the heat of reaction. Heat liberated by the hydriding reaction sintered the hydride into granular frits. These frits ranged in size up to 1/8 of an inch; a large fraction fell in the size range from 1/16 to 1/8 of an inch. Occasionally, heat of reaction caused the frit to glow a dull red.

Frit size decreased only slightly for very slow reaction rates. When the supply rate of hydrogen was cut from 1200 cc per minute (the maximum rate of hydrogen uptake) to less than 40 cc per minute, the frit came off in slightly smaller pieces. The longer reaction period did not, however, justify the slight decrease in particle size.

Temperature had little effect upon the rate of hydriding in the temperature range from 50 to 250 C. The reaction rate appeared to drop off sharply, however, at 250 C.

Size and shape of the starting metal were varied to determine their effect upon size range and distribution of the hydride particles. Thin metal plates, 1/8-inch metal balls, and metal "buttons" one-inch in diameter by half an inch thick were used. Size characteristics of the metal had little effect on the resultant hydride.

Another attempt at size reduction was multiple cycling. The metal frit was hydrided and dehydrided several times in an effort to reduce the large particles into a fine powder. After several cycles, however, the large pieces still remained. Metal formed by decomposing the hydride

was porous and failed to subdivide further during subsequent hydriding reactions.

Plutonium metal becomes porous when cycled thermally between two or more crystal phases. A decrease in density of nearly 25 percent can be obtained by cycling metal fifty times between room temperature and 180 C.⁽⁸⁾ When hydrided, this porous metal might form smaller hydride frits than ordinary metal does. No decrease in particle size occurred for hydride prepared from metal which had been cycled 18 times, but investigation of more extensive cycling may be justified. The metal which had been cycled 15 times resisted initiation to hydriding, as compared to freshly-cast metal, probably due to altered structure, or due to increased surface oxidation.

Particle size of the hydride would probably be smaller if it were prepared in a revolving, stainless steel combustion tube. Less sintering would occur in a metal tube which would conduct away the heat of reaction. The revolving action would minimize sintering and would tend to break up the frit. Because it does not hydride, stainless steel is suggested as the material of construction.

Another hydriding procedure⁽⁹⁾ which was investigated consists of the following steps:

1. Visible, loosely-adhering oxide was removed from the surface of the metal. The metal was cleaned in one of three ways: (a) with a wire brush, (b) with a hot solution of 0.005 M hydrofluoric acid in nitric acid, or (c) by vacuum casting.
2. The metal was scratched lightly with an emery cloth.
3. It was heated to 100 C, then cooled to about 50 C under continuous vacuum.
4. The metal was reacted with dry, oxygen-free hydrogen at room temperature.

The disadvantage of this method was the emphasis placed upon surface purity of the metal. A time lag always occurred between the introduction of hydrogen and the start of the hydriding reaction. This lag or induction period varied from a few minutes to a few hours, depending upon the surface purity of the metal. The induction period for metal cleaned by pickling or vacuum casting was roughly five minutes. Surfaces cleaned with a wire brush reacted after a period of about 20 minutes. Sometimes the metal failed to react after several hours. Occasionally the reaction stopped after a black coating had formed on the outside of the metal; the reaction was brought to completion by out-gassing the metal and then heating it in hydrogen until the reaction restarted.

In another variation of this process, a stream of mixed hydrogen

and argon was passed over the reacting metal. This procedure decreases the rate of reaction and removes heat of reaction. Trace impurities, in the large volume of gas used, caused oxidation, rather than hydriding, of the metal.

C. The Decomposition Of Plutonium Hydride

The rate of decomposition of plutonium hydride is a function of both temperature and pressure⁽⁶⁾⁽⁷⁾ (see Figure 3⁽¹⁾). At any given temperature, if the pressure is reduced just below the dissociation pressure, some of the hydride will dissociate until equilibrium is obtained. If the evolved hydrogen is continuously removed, the decomposition will proceed to completion.

In practice, the hydride was decomposed at 400 C and a pressure of three microns. No visible change occurred; the granular metal frit had the same size, shape, and color as the original hydride. The metal was brittle and could easily be crushed. A lower decomposition temperature would have been desirable to avoid sintering of the powder, but pressure limitations made this impossible.

Sintering is a function of time, temperature, particle size, and purity.⁽²⁾ Sintering of the metal powder was investigated by decomposing hydride at a given temperature for 45 minutes. Beads of metal appeared in the sinter at about 500 C. Agitation of the powder, by a vibrator, seemed to postpone sintering until about 400 C.

D. Pyrophorocity

In powder form, both plutonium metal and plutonium hydride are highly pyrophoric.⁽²⁾ In the interest of fire safety, both of these powders were exposed to the inert atmosphere surrounding the apparatus in which they were prepared. This atmosphere was argon which contained enough air to analyze from one to two percent oxygen. Neither the metal nor the hydride ignited upon exposure. Apparently, the oxidation rate was slow enough to prevent ignition. Later, the same powders were exposed to an air atmosphere. Again, the powders failed to catch fire. A fire occurred, however, in an air atmosphere when the hydride particle size distribution determination was being performed. This hydride did not burn on being screened, but upon being brushed by a camel hair brush. Apparently little fire hazard exists when these powders are prepared or stored in an inert atmosphere glove box.

E. Apparatus For The Production Of Plutonium Powder On A 500-Gram Scale

Experimental data suggests an apparatus similar to that shown in Figure 4 for powder production on a 500-gram scale.

A framework "B", which could be rotated in a vertical plane, would support the apparatus. The combustion tube "A" would consist of two stainless steel tees welded to a short length of stainless steel pipe. One end of the tube would be supported by a modified glass-blowers' support, "F". The other end would be supported by a closed-end piece of stainless steel tube (a thermowell), "D", which passes through a single row radial bearing "E" mounted on the framework. Washers welded onto the thermowell, together with the bearing, would prevent tube motion in the horizontal direction. The tube would be rotated by means of a gear wheel "G" and an electric motor, "H". Blades attached to the inside wall of the tube would tumble the powder during rotation. Vacuum line "C" enters the tube through a rotary vacuum seal in the end plate. A flange welded onto the inside tee would provide the base for an observation port.

To load the apparatus, the window from the observation port would be removed and metal inserted into the tube. Powder would be retained in the tube, during rotation, by inclining it below the horizontal.

Powder would be unloaded by attaching a receiver, "L", to the apparatus, opening the ball valves, "J", and then tilting the tube upward. Powder would slide into a collecting funnel, "N", and drop down into the receiver. The funnel would consist of a piece of stainless steel pipe welded onto a flanged weld cap. The receiver would be attached to the apparatus by means of quick vacuum couplings, "L", and a connecting tube. The receiver would consist of a section of stainless steel pipe with an observation port on one end and a ball valve and quick vacuum coupling on the other end. The receiver would be removed from the apparatus during operation, and the coupling plugged. Large particles would be retained in the apparatus by a 200-mesh screen inserted between the cap and the tee.

The furnace, "R", would be held at the decomposition temperature of 400 C. The hydriding reaction would be initiated by putting the furnace into place with block "M". Temperatures would be measured with a chromel-alumel thermocouple. A clamp attached to the framework would keep the thermocouple from rotating and would hold it inside the thermowell.

The combustion tube could be used as a ball mill by inserting stainless steel or plutonium balls. Stainless steel balls will not hydride⁽³⁾ and could remain in the apparatus during the entire operating cycle. Plutonium balls could be formed from the feed metal by only partially hydriding it, or they could be inserted after the hydriding step.

V. FUTURE WORK

Purity of the metal powder could be determined from x-ray diffraction studies. Diffraction patterns could show what fraction of the metal was oxidized during the hydriding process. A sample of hydride could be exposed to the hood atmosphere for a short period of time; the degree of

oxidation would determine the feasibility of introducing plutonium balls (for grinding purposes) into the 500-gram scale apparatus during the process.

Thermal cycling of the feed metal could be investigated more thoroughly. The effect on hydride particle size of thermally-cycled feed metal could be determined for metal which had been cycled at least 50 times from room temperature to 180 C.

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TABLE IDIFFERENTIAL SCREEN ANALYSIS
FOR THE PLUTONIUM HYDRIDE FRIT

<u>MESH</u>	<u>CLEAR OPENING -</u> <u>mm</u>	<u>WEIGHT %</u>
+ 14	1.168	50.0
+ 32	0.495	28.7
+ 60	0.246	9.5
+115	0.124	5.6
+270	0.053	3.7
-270		2.5

FIGURE 1

EXPERIMENTAL APPARATUS

- A. Vycor Combustion Tube
- B. Electric Furnace
- I. Glass Vial
- O. Stainless Steel Thermowell
- Y. 60 Cycle Vibrator
- Z. Vacuum Line

FIGURE 2

EXPERIMENTAL APPARATUS

A. Vycor Combustion Tube	M. Closed Tube Manometer
B. Electric Furnace	N. McLeod Gauge
C. Temperature Recorder-Controller	P. Oil Diffusion Pump
D. Variac	Q. Mechanical Vacuum Pump
E. Argon Recirculation System	R. Dust Trap
F. Gas Analyzer	S. Scrubber
G. Hydrogen Bottle	T. Air Jet Ejector
H. "Deoxyo" Palladium catalyst	U. Pressure Regulator Valve
J. Drying Column	V. Vacuum Gauge
K. Argon Bottle	W. Bellows Valve
L. Bed Of Copper Turnings	X. Rotameter

FIGURE 3

Various Stages of the Hydriding Process

- A. Oxidized Plutonium Button.
- B. Clean Plutonium Button.
- C. Partially-hydrated Metal.
- D. Metal Frits After Several Hydriding Cycles.
- E. Metal Frits.
- F. Hydride Frits.

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FIGURE 4

THE DECOMPOSITION PRESSURE OF PLUTONIUM DIHYDRIDE (1)

FIGURE 5

PROPOSED APPARATUS FOR THE PRODUCTION OF PLUTONIUM POWDER
ON A 500-GRAM SCALE

- A. Combustion Tube
- B. Framework
- C. Vacuum Line
- D. Thermowell
- E. Single Row Radial Bearing
- F. Glass Blower's Support
- G. Gear Wheel
- H. Electric Motor
- J. Ball Valve
- K. Quick Vacuum Coupling
- L. Receiver
- M. Supporting Block
- N. Collecting Funnel
- P. Connecting Tube
- R. Electric Furnace