LA-6681-MS
Informal Report

UC-4

Issued: July 1977

The Reaction Between Plutonium and Deuterium
Part II. Rate Measurements by Weight Changes

David F. Bowersox

los alamos
scientific laboratory
of the University of California
LOS ALAMOS, NEW MEXICO 87545

UNITED STATES
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
CONTRACT W-7405-ENG. 36

Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161
Price: Printed Copy $3.50 Microfiche $3.00

THE REACTION BETWEEN PLUTONIUM AND DEUTERIUM
PART II. RATE MEASUREMENTS BY WEIGHT CHANGES

by

David F. Bowersox

ABSTRACT

The effects of pressure and temperature upon the rate and mechanism of the reaction between plutonium and deuterium have been studied for temperatures to 400°C at pressures from 1 to 15 kPa. The rate was determined by measuring the weight changes of plutonium disks as the reaction proceeded. Below 200°C the reaction product spalled to expose fresh metal. The equation $R = k_T A P^{0.6}$ fits the data, where the rate R is the milliequivalents of deuterium reacting per hour, A is the geometrical surface area, P is the deuterium pressure, and k_T is the velocity constant at temperature T. The energy of activation for the spalling reaction is 5.9 $kcal \cdot mol^{-1}$ for $PuD_{2.7}$.

Between 250 and 400°C the product adhered to the parent metal to form a growing layer. The equation $R = k_T^* AP/\Delta W$ fits the rate data, where R, A, and P are defined above, ΔW is the measured weight change in milliequivalents of deuterium, and k_T^* is the velocity constant at temperature T.

I. INTRODUCTION

Studies of the hydriding of metals have been hampered by lack of purity in both metals and gases, by insufficient care in obtaining reproducible surfaces, and by inaccurate temperature control. The rate of hydrogen sorption depends strongly on the presence and porosity of an impeding nonmetallic layer such as an oxide or nitride. Hydriding is not observed until enough gas has diffused through the coating and reacted with the parent metal to form a product that cracks the coating to expose the metal. Exothermic hydriding often causes localized heating and a subsequent rapid increase in the hydriding rate. I have found evidence of this heating and rate increase in the hydriding of plutonium (Ref. 1).

Plutonium and hydrogen react to form a separate phase of dihydride.[2] After all the plutonium is converted to dihydride, additional hydrogen forms a solid solution up to the trihydride composition. However, the hydrogen content of stable hydrides decreases with increasing temperature from 150 to 400°C. Powdered $PuH_{2.7}$ forms by direct reaction at 150°C (Ref. 3), whereas at 400°C, the product is $PuH_{2.1}$ (Ref. 1).

Studies of plutonium hydrides have been concerned with hydriding of the metal during storage and nonuniform or slow hydriding upon exposure of plutonium to hydrogen gas. A tarnish of either hydride or oxide forms on the metal in dry air during storage and evidently inhibits further reaction.[4] In moist air, however, the tarnish is unstable and extensive reaction occurs.

In an earlier study I determined the hydriding rate by measuring the changes in gas pressure as the reaction proceeded.[5] The problems encountered were sufficient to justify a second study. For example, pressures decreased very rapidly during the first few minutes, and so many of the rate measurements were made after most of the gas had reacted. The resulting rate decrease was particularly pronounced above 200°C. The deuterium concentration, or the pressure, is one of the variables that controls the rate, and so these changes could cause errors in the rate equations. Below 150°C rapid hydriding caused temperature spikes at pressures at which the pressure changes could be measured conveniently.

In this study I determined the rate by measuring changes in the specimen weight as the reaction proceeded at constant temperature and pressure. Temperature changes were minimized by using thin disks of plutonium bonded to beryllium to provide rapid dispersal of heat and by hydriding at low reaction rates. The experiments were conducted in an inert glove box to minimize oxidation.

II. EXPERIMENT

A. Materials

Disks of delta-stabilized 1-wt% Ga-Pu alloy bonded to 2.5- by 1.5-cm right cylinders of beryllium* were used for all the hydriding experiments except the ones concerning the effects of composition and area changes. These specimens provided a well-defined geometrical surface area and a large heat sink to withdraw most of the heat generated by the reaction. Each disk was vacuum annealed at 300°C for at least 12 h to produce a uniform surface that hydrided reproducibly.[5]

The effects of composition upon rate were determined by hydriding bonded disks of 1-wt% Ga-Pu alloy and 25- by 6- by 0.6-mm-thick coupons of electrorefined plutonium. Powders of characterized sizes, disks, and coupons of 1-wt% Ga-Pu alloy were hydrided to determine how geometrical surface area affects the rate.

High-purity deuterium was further purified in a heated palladium-alloy hydrogen diffusion cell and stored in 1-ℓ stainless steel tanks before use.

B. Equipment

The plutonium was stored and hydrided in a small glove box (160 cm wide by 76 cm deep by 100 cm tall) filled with argon and maintained at less than 10 ppm of oxygen and water by a Dri-Train* system. Both hydride and plutonium were stable in this atmosphere and oxidation was not observed during storage.

A semimicro balance in the glove box was enclosed by a large bell-jar and the balance case floor. Lines connected the balance chamber to a vacuum system and supplies of purified argon and deuterium. The balance chamber was also connected to a reaction chamber, a 45-cm-long by 5-cm-o.d. Pyrex tube directly below the left balance pan. Both chambers formed the reaction system, which was always maintained at a selected pressure. The lower section of the reaction chamber could be heated to 450°C by a 15-cm-long by 5-cm-i.d. tube furnace. A 5.2-cm-long by 3.2-cm-o.d. tantalum reaction crucible was suspended from the left balance pan by a tungsten wire into the center of the Pyrex-tube section heated by the furnace.

Weight changes were balanced by automatic addition of weights to the right balance arm in 10-mg increments to a maximum of 1 g. Changes of as little as 10 mg were recorded on a strip chart. A Servo amplifier** measured the pressures in the reaction system. Temperatures were measured 1 cm below the reaction crucible by Chromel-Alumel thermocouples† and were controlled to 2° by an external controller. In tests, temperatures there were within 2° of those at the sample surface.

C. Procedure

Each metal specimen was cleaned and stored in the inert glove box. The specimen for each experiment was placed in a reaction crucible. After the sample had been weighed, the entire reaction system was evacuated to 10^{-7} kPa and then heated to 300°C for 20 h.

The temperature was adjusted and maintained at the value selected for hydriding in that experiment.

---

*The bonded disks were provided by Roland Fisher of the Rockwell International Rocky Flats Plant, Golden, CO.

*Model HE-193-2 Dri-Train, Vacuum/Atmospheres Co., Hawthorne, CA 90250.

**Type 1-169-0001, Bell and Howell Co., Pasadena, CA 91109.

†Hoskins Manufacturing Co., Detroit, MI 48208.

After 1 h at temperature, deuterium was introduced into the system. Pressure and weight were recorded throughout the experiment, usually for 4 to 8 h. Pressures were varied over a number of selected values at each temperature. Adjustments in the reaction system pressure were made by manually admitting or withdrawing small increments of deuterium.

After each hydriding experiment was completed, the reaction chamber was evacuated and cooled to room temperature. The product was examined, photographed, and then oxidized before transfer for plutonium recovery.

Data were collected during the entire reaction, but calculations of rate were performed with the data taken during the first half of the total reaction time to reduce errors that might result from changes in surface area. Actually, calculations showed that surface areas decreased slowly. Calculated rates were not affected by area changes for almost 90% of the reaction interval. Temperature variations during reaction were minimized by the use of low hydriding rates and bonded samples.

The rate of reaction was calculated by dividing the weight change, in milliequivalents, by the time interval between weight readings. Changes in weight could be read to an accuracy of 0.0002 g, and time intervals were taken from the chart strip to an accuracy of at least ±2 s. Geometrical surface areas were calculated from the dimensions of the samples. Pressures were displayed to ±0.02 kPa on a strip chart.

III. RESULTS

A. The Reaction Product

The reaction between deuterium gas and plutonium proceeded as observed in the previous study.[5] Below 200°C the product spalled from the surface to form a granular powder. As the reaction temperature was increased, the product gradually changed to metallic platelets between 200 and 250°C. Above 250°C the product adhered to the parent metal with little change in the appearance of the metal. This product layer was stable and, once formed, interfered with the spalling reacion.

The mechanism and rate of reaction apparently changed with the physical form of the product. The rate of the spalling reaction increased with increasing temperature. At constant temperature and pressure, this rate was independent of time. Above 200°C, the rate of the adhering reaction was fairly constant over a range of temperatures. However, at constant pressure, the rate decreased rapidly with time. Therefore, the experimental data could be divided into two general patterns of behavior corresponding to the two physically different reaction products. These reactions will be discussed separately in the next two sections.

B. The Spalling Reaction

Powders, disks, and coupons were hydrided at 150°C and 1.5 kPa to determine the effect of surface area on the rate of spalling. The surface area was assumed to be approximately equal to the geometrical area for these samples under the hydriding conditions. The data summarized in Table I show that the ratio of the rate to area is fairly constant over a large change in area. Variations in the ratio are probably due to errors in equating geometrical to actual surface area. The data, therefore, show that the hydriding rate is directly proportional to the surface area.

In additional experiments at constant area and pressure, rates were independent of reaction time at 150°C (see Table II). Finally, the rate was determined as a function of pressure. Results at 150°C, as given in Table III, clearly indicate that the rate is proportional to the pressure to the 0.6 power. Data collected over a series of pressures and temperatures verified the 0.6 dependence of the rate on the pressure (see Table IV).

Under these experimental conditions, the rate R ($\mathrm{meq \cdot h^{-1}}$) can be expressed by the equation

$$R = k_T A P^{0.6} \qquad (1)$$

where A is the surface area ($\mathrm{mm^2}$), P is the pressure (kPa) and k_T is the velocity constant ($\mathrm{meq \cdot mm^{-2} \cdot kPa^{-0.6} \cdot h^{-1}}$) at temperature T. The values for k_T were calculated from rate data collected over the temperature range 50 to 200°C. These constants (summarized in Table V) increased with temperature from 0.069 at 50°C to 0.181 at 200°C.

TABLE I

RATE OF HYDRIDING AT 150°C AND 1.5 kPa VS AREA

Surface Area (mm^2)	Rate (meq/s)	Rate/Area ($meq/s \cdot mm^2$)
95	0.40×10^{-3}	4.2×10^{-6}
360	1.7×10^{-3}	4.7×10^{-6}
860	4.1×10^{-3}	4.8×10^{-6}
1260	5.5×10^{-6}	4.3×10^{-6}

TABLE II

RATE OF HYDRIDING AT 150°C AND 2.6 kPa VS TIME[a]

Total Time (min)	Weight Change (meq)	Rate (meq/s)
22.3	5	3.73×10^{-3}
44.9	10	3.71×10^{-3}
67.5	15	3.70×10^{-3}
90.1	20	3.69×10^{-3}
112.3	25	3.71×10^{-3}

---

[a] The sample is a 2.5-mm-diam disk of 1-wt% Ga-Pu alloy bonded to a 25- by 25-mm right cylinder of Be.

TABLE III

RATE OF HYDRIDING AT 150°C VS PRESSURE[a]

Pressure (kPa)	Rate (meq/s)	Slope, n[b]
2.62	3.13×10^{-2}	---
5.51	5.21×10^{-2}	0.68
7.81	6.30×10^{-2}	0.63
10.5	7.55×10^{-2}	0.63
12.9	8.95×10^{-2}	0.65
		Av = 0.065 ± 0.02

---

[a] The sample is a 25-mm-diam disk of 1-wt% Ga-Pu alloy bonded to a 25- by 25-mm right cylinder of Be.

[b] Slope, $n = [\log R_x - \log R_1]/[\log P_x - \log P_1]$, where n is the calculated order of the reaction with respect to pressure and the subscript indicates the x^{th} experimental value.

TABLE IV

PRESSURE DEPENDENCE VS TEMPERATURE FOR THE SPALLING REACTION[a]

Temperature (°C)	Pressure Range (kPa)	Slope, n[b]
50	2.0 - 13.4	0.61
75	0.7 -12.5	0.69
100	2.1 - 11.0	0.61
125	0.4 - 9.8	0.57
150	2.6 - 12.9	0.65
200	1.9 - 5.6	0.75[c]

---

[a] The samples are 25-mm-diam disks of 1-wt% Ga-Pu alloy bonded to 25- by 25-mm right cylinders of Be.

[b] Slope, $n = [\log R_x - \log R_1]/[\log P_x - \log P_1]$, where n is the calculated order of the reaction with respect to pressure and the subscript indicates the x^{th} experimental value at a given temperature.

[c] There is evidence that the rate is decreasing with time in this experiment.

TABLE V

VELOCITY CONSTANTS FOR THE SPALLING REACTION[a]

Temperature (°C)	k_T [b] ($meq \cdot mm^{-2} \cdot kPa^{-0.6} \cdot h^{-1}$)
50	0.069 ± 0.006
75	0.089 ± 0.0012
100	0.110 ± 0.009
125	0.112 ± 0.003
150	0.131 ± 0.004
200	0.181 ± 0.012

---

[a] The samples are 25-mm-diam disks of 1-wt% Ga-Pu alloy bonded to 25- by 25-mm right cylinders of Be.

[b] Velocity constant, $k_T = R/AP^{0.6}$.

The pressure dependency of the spalling reaction fits a mechanism having a steady-state intermediate product. If it is assumed that diffusion of gas to the Pu/D_2 interface and of products away from the interface is relatively rapid, the rate-controlling steps will then be formation and reaction of such an intermediate. A series of reactions may be postulated,

$$\mathrm{Pu} + 1/2\,\mathrm{D_2} \xrightarrow[k_1]{} \mathrm{PuD} \qquad (2)$$

$$\mathrm{PuD} \xrightarrow[k_{-1}]{} \mathrm{Pu} + 1/2\,\mathrm{D_2} \qquad (3)$$

$$\mathrm{PuD} + 1/2\,\mathrm{D_2} \xrightarrow[k_2]{} \mathrm{PuD_2}\ , \qquad (4)$$

where k_1, k_{-1}, and k_2 are the velocity constants for the individual reaction steps. If the species PuD is an active intermediate which can either decompose or react with more deuterium to form dihydride, the rate expression becomes

$$R = d(\mathrm{PuD_2})/dt = k_2(\mathrm{PuD})(\mathrm{D})^{1/2} \qquad (5)$$

Under a steady-state assumption

$$d(\mathrm{PuD})/dt = k_1 A(\mathrm{D})^{1/2} - k_{-1}(\mathrm{PuD}) - k_2(\mathrm{PuD})(\mathrm{D})^{1/2} = 0\ . \qquad (6)$$

If the terms are rearranged, Eq. (6) becomes

$$(\mathrm{PuD}) = k_1 A(\mathrm{D})^{1/2}/[k_{-1} + k_2(\mathrm{D})^{1/2}]\ , \qquad (7)$$

and from Eq. (5) and (7)

$$R = d(\mathrm{PuD_2})/dt = k_2 k_1 A(\mathrm{D})/[k_{-1} + k_2(\mathrm{D})^{1/2}]\ . \qquad (8)$$

If the term $k_2(\mathrm{D})^{1/2}$ is much less than k_{-1}, the rate will be first order with respect to the deuterium concentration. This can occur if k_{-1} is very large relative to either k_2 or $(\mathrm{D})^{1/2}$. On the other hand, if the product $k_2(\mathrm{D})^{1/2}$ is much larger than k_{-1}, the reaction order will be 0.5. This can occur if k_2 or $(\mathrm{D})^{1/2}$ is very large relative to k_{-1}. The rate expression is then the same as for the classical diatomic gas reaction. Finally, if k_{-1} is approximately equal to the product $k_2(\mathrm{D})^{1/2}$, the deuterium dependency can vary. The data indicate that this equality probably exists in the pressure range examined.

The data can be interpreted with other mechanisms such as mixed attack by atomic and molecular deuterium at the metal-gas interface, or diffusion of molecular and atomic deuterium through either an oxide or hydride coating of constant thickness. At pressures higher than those in this study the slow reaction could be the rate of diffusion of deuterium from the bulk gas to the metal-gas interface without changing my interpretation in this study.

If the velocity constant is converted from pressure-dependent terms to concentration units, the energy of activation for Eq. (1) can be calculated from the equation

$$\Delta H_a = \log\,(k'_T/k'_{T_0})\ [2.303\ RTT_0/(T - T_0)]\ , \qquad (9)$$

where the k'_T values are the concentration-dependent velocity coefficients. The activation energy is 2.2 ± 0.1 $\mathrm{kcal\cdot mol^{-1}}$, which corresponds to 5.1 $\mathrm{kcal\cdot mol^{-1}}$ for $\mathrm{PuD_{2.8}}$ and 5.9 $\mathrm{kcal\cdot mol^{-1}}$ for $\mathrm{PuD_{2.7}}$. This agrees with the value of 6.1 $\mathrm{kcal\cdot mol^{-1}}$ reported by the British for plutonium deuteride.[6]

The steady-state equations indicate that at sufficiently high pressures the reaction in Eq. (4) should predominate and the order of the reaction with respect to deuterium should become 0.5. At high pressure the rate of hydriding would be so rapid that heat transfer would probably not be sufficient to remove all the reaction heat. Localized heating would occur and cause an increasing rate of reaction (as reported in Ref. 6 and 7). Therefore, be careful when using Eq. (1) to predict hydriding rates from experiments where temperature is not controlled.

C. The Adhering Reaction

At 200°C the reaction product partially adhered to the parent metal. At constant pressure, the reaction rate decreased parabolically with time. The time-rate profile was similar to that for the classical case of a solid-state reaction in which a solid product layer is formed. Here the rate of transport of the reacting species across the phase boundaries and through the product layer usually determines the rate of reaction. Because the surface area is constant and the rate of growth of the product is measured, the rate parameters could be determined quite accurately.

The parabolic rate law, which often applies to high-temperature corrosion reactions, apparently fits the adhering reaction. The basic assumption is that thermodynamic equilibrium is maintained at the interfaces, that is at the $\mathrm{Pu/PuD_2}$ and $\mathrm{PuD_2/D_{2\,(g)}}$ phase boundaries, and throughout the compact, strongly adherent product layer. The driving force for gas diffusion through the product layer then is inversely proportional to the product layer thickness, Δx, at any time. The instantaneous rate of increase in thickness, $d(\Delta x)/dt$, can then be expressed as $1/\Delta x$; and so, at constant temperature and pressure,

$$d(\Delta x)/dt = 1/\Delta x \quad . \tag{10}$$

Integrating Eq. (10) gives the parabolic rate law as

$$\Delta x^2 = 2\, k_T{}^* t \quad , \tag{11}$$

where $k_T{}^*$ is the velocity constant at temperature T.

The correctness of Eq. (11) was tested during a series of rate experiments. The reaction rate was initially quite rapid, then slowed as the weight of product, ΔW, increased. If all the product adheres uniformly, ΔW is proportional to the product layer thickness. Plots of ΔW^2 vs time were linear; therefore the parabolic rate law holds. Calculations from my experimental data using Eq. (11) showed that the rate was directly proportional to the pressure between 250 and 400°C. This pressure dependency was not detected in the earlier hydriding study.[5] Rapid decreases in pressure and the build-up of a product layer masked the pressure effect in those experiments.

Thus the rate expression for the adhering reaction is

$$R = k_T{}^* AP/\Delta W \tag{12}$$

where $k_T{}^*$ is the velocity constant ($\text{meq}^2 \cdot \text{mm}^{-2} \cdot \text{kPa}^{-1} \cdot \text{h}^{-1}$) at temperature T, A is the area (mm^2), P is the pressure (kPa), and ΔW is the weight gain (meq). The values of $k_T{}^*$ calculated from the experimental data are given in Table VI. Note that there is little change in the velocity constant from 300 to 400°C.

D. Effect of Alloy Composition

The rate and mechanism of the hydriding reaction changed with the alloy compositon of the metal specimens. Disks of electrorefined plutonium and delta-stabilized 1-wt% Ga-Pu alloy were hydrided at a variety of temperatures and pressures to determine these changes. The pressure dependency for each composition in given as a function of temperature in Table VII. The pressure dependency increases from 0.6 for the spalling reaction at lower temperature to 1.0 for the adhering reaction at higher temperatures. The transition occurs at about 100°C for electrorefined metal, and 200°C for 1-wt% Ga-Pu alloy.

The rates of hydriding at 50°C, where the spalling reaction predominates, are similar for both compositions. The rate decreased very rapidly in each case when the adhering reaction began to control the rate. Finally, above 250°C, the rates for both compositions again were nearly equal.

TABLE VI

VELOCITY CONSTANTS FOR THE ADHERING REACTION[a]

Temperature (°C)	k_T[b] ($\text{meq}^2 \cdot \text{mm}^{-2} \cdot \text{kPa}^{-1} \cdot \text{h}^{-1}$)
250	0.20
300	0.12
350	0.11
400	0.14

[a] The samples are 25-mm-diam disks of 1-wt% Ga-Pu alloy bonded to 25- by 25-mm right cylinders of Be.

[b] Velocity constant, $k_T = R\, \Delta W/AP$.

IV. CONCLUSIONS

The complexity of the hydriding reaction is due to the change in mechanism and the change in pressure dependency. The hydrogen concentration dependency for the spalling reaction can vary from 1.0 at low pressures to 0.5 at high pressures. Therefore at high pressures, a typical diatomic gas-metal reaction occurs, and at low pressures a molecular reaction takes place.

The activation energy for the spalling reaction is about 6 kcal·mol⁻¹ and the heat of formation of the dihydride is estimated to be −3.5 kcal·mol⁻¹ (Ref. 8). The heat released by the reaction probably

TABLE VII

PRESSURE DEPENDENCE OF THE HYDRIDE REACTION FOR TWO SAMPLE COMPOSITIONS VS TEMPERATURE

Temperature (°C)	Electrorefined Pu	1.0-wt% Ga-Pu
50	0.6	0.6
100	0.8	0.6
150	1.0	0.6
200	1.0	0.8
250	1.0	1.0
350	1.0	1.0

causes the rapid increase in temperature and rate that has been observed.[7] As a localized area reacts, the temperature would rise because of the poor heat conductivity of the metal. As the temperature rises, the rate would increase. Thus more heat would be generated and the temperature and rate would continue to increase. This increase has been attributed to a catalytic reaction rather than to the exothermic nature of the hydriding.[9] In this study, in which temperatures were maintained at constant values, no catalysis was observed.

ACKNOWLEDGMENTS

I thank R. M. Alire of this Laboratory for his encouragement and helpful discussions during this study.

REFERENCES

1. D. F. Bowersox, Los Alamos Scientific Laboratory, unpublished data, May 1974.

2. I. B. Johns, "Plutonium Hydride and Deuteride," Atomic Energy Commission report MDDC-717 (June 1944).

3. C. F. Brown, M. M. Ockenden, and G. A. Welch, J. Chem. Soc., 1955:3932.

4. A. S. Coffinberry, F. W. Schonfeld, J. T. Waber, L. R. Kelman, and C. R. Tipton, Jr., "Corrosion and Oxidation," in *Reactor Handbook,* 2nd ed., C. R. Tipton, Jr., Ed. (Interscience Publishers, Inc., New York, 1960), Vol. I, pp. 145-190.

5. D. F. Bowersox, "The Reaction Between Plutonium and Deuterium, Part I. Rate Measurements by Pressure Changes," Los Alamos Scientific Laboratory report LA-5515-MS (May 1974).

6. Robin Horscroft, United Kingdom Atomic Energy Authority, Research Group, Harwell, private communication, May 1975.

7. W. M. Olson, Los Alamos Scientific Laboratory, private communication, January 1974.

8. R. N. R. Mulford, Los Alamos Scientific Laboratory, private communication, July 1976.

9. J. W. Ward, Los Alamos Scientific Laboratory, private communication, September 1973.