Journal of Alloys and Compounds, 187 (1992) 271–283
JALCOM 293

Kinetics for the reaction of hydrogen with plutonium powder

Jerry L. Stakebake
EG&G Rocky Flats Inc., Golden, CO 80402 (USA)

(Received December 16, 1991; in final form March 9, 1992)

Abstract

The rate of hydriding of plutonium powder was measured over the temperature range −41 to 350 °C and at hydrogen pressures of 0.007, 0.07 and 26.5 kPa. Two kinetic models were evaluated and discussed. Hydriding rates were independent of temperature over the entire temperature range. The hydriding rates were also independent of hydrogen pressure above 1 kPa. At lower pressures, the hydriding rates followed two different types of pressure dependence. A pressure dependence of $P^{1/2}$ was found in the range $1 > P > 0.07$ kPa and at low pressure ($P < 0.07$ kPa) the rate of hydriding was proportional to P^1. The results indicate adsorption-controlled kinetics at low hydrogen pressures whereas the kinetics are reaction controlled at high pressures.

1. Introduction

Hydriding reactions involving plutonium and plutonium alloys have received relatively little attention and as a result are not completely defined. This is particularly true in areas such as reaction kinetics and mechanisms. Available information on all aspects of plutonium hydride chemistry has been reviewed by Haschke [1]. Allen [2] has recently investigated the solubility of hydrogen in the temperature range 475–825 °C and points out several areas requiring further study. Early kinetic studies [3–5] focused on the measurement of the kinetics for hydriding bulk plutonium samples. In these studies, the initial kinetics were characterized by variable induction times and an accelerating stage during which hydride nucleation occurred. To eliminate the induction period, samples were activated by either heating in vacuo to 300 °C [3, 4] or prehydriding [5] a portion of the sample. Prehydriding removed the oxide layer on a small area by spallation and left a thin oxide-free hydride layer on the surface.

Reaction induction time was eliminated in an earlier study by the author [6] by using a powdered plutonium alloy prepared in situ by the decomposition of the hydride under vacuum. In this study a plutonium–1wt.% gallium alloy was used and the reaction kinetics were measured between −29 and 355 °C at pressures between 0.02 and 67.96 kPa. The first-order hydriding rates exhibited a hydrogen pressure dependence that could be described by a modified Langmuir equation. The reaction was non-isothermal and several

0925-8388/92/$5.00

questions were posed regarding the lack of a temperature dependence for the rate of hydriding. It was concluded in this study that the similarity of the rates over a 384 °C temperature range was sufficient to justify the claim of a temperature-independent reaction.

This paper is a report of the results obtained from the investigation of the hydriding of pure plutonium powder. Kinetics for this reaction are presented and the results are compared with those previously [6] reported for alloyed plutonium.

2. Experimental details

2.1. *Materials*

The plutonium used for these studies was unalloyed. Table 1 summarizes the impurity content of the metal with the exception of ^{241}Am. A small percentage of ^{241}Pu was present in the plutonium, which was primarily ^{239}Pu. ^{241}Pu has a 13-year half-life and decays to ^{241}Am. Therefore the plutonium will have contained americium concentrations varying with time. Individual samples weighing approximately 1.5 g were prepared by mechanically polishing to remove the oxide layer and were immediately transferred to the vacuum microbalance. Ultrapure hydrogen (99.999%) was used in this investigation and was introduced into the system through a heated bed of uranium hydride to reduce oxygen contamination further.

2.2. *Apparatus*

The experimental system utilized a vacuum microbalance to perform the thermogravimetric kinetic measurements. This system was described in detail earlier [7]. Minimum pressures attainable were in the 10^{-6} Pa range. Hydrogen pressures were controlled with a Granville–Phillips pressure controller and could be varied from 10^{-4} to 10^{5} Pa. Sample temperatures were measured

TABLE 1

Chemical analysis of plutonium samples

Element	Concentration (ppm)	Element	Concentration (ppm)
Al	46	P	2.2
Cl	0.7	Pb	12
Cr	50	S	4.6
Cu	0.9	Si	23
F	2.4	Ta	26
Fe	96	V	0.2
Ga	72	Zn	35
Mg	1.1		
Mn	21		
Ni	68	Total	461.1

with a thermocouple located adjacent to the sample. Outputs from the microbalance, thermocouples and pressure meters were collected with a computer-controlled data acquisition system.

2.3. *Procedure*

Plutonium powder was prepared by repeatedly hydriding and then dehydriding a 1.5 g plutonium sample. In order to eliminate the induction time for hydriding, the coupon was prenucleated by exposure to 2.7 kPa of hydrogen at 25 °C until 0.1–0.3 mg of hydrogen had reacted. The system was then evacuated and the bulk coupon was hydrided at 25 °C in 0.07 kPa of hydrogen. These initial hydriding conditions produced the maximum surface area for the powder. Plutonium metal powder was formed by decomposition of the hydride under vacuum at 480 °C and outgassing to a final pressure of 10^{-6} Pa. Surface areas of the powders were measured using the BET technique of argon adsorption at -196 °C [8]. Nitrogen adsorption could not be used on the hydride because of its reactivity to form the nitride. Kinetics for plutonium powder hydriding were measured over the temperature range -41 to 350 °C and at hydrogen pressures of 0.007, 0.07 and 26.5 kPa. Following each run, the sample was dehydrided at 480 °C and reused for the next hydriding run. Six different bulk plutonium samples were used with 2–12 runs being made on each sample. Repeated runs on any one sample had no effect on the surface area of the powder or the reaction rates observed.

3. Kinetic models

Evaluation of the hydriding kinetics involved the consideration of two fundamental reaction processes: (1) the chemical reaction itself and (2) transport of the hydrogen to the reaction zone. Two basic kinetic models, "progressive conversion" and "phase boundary", were considered in this work [9]. The basic assumption of the progressive conversion model is that the hydrogen diffuses rapidly through the solid particle so that the hydriding reaction occurs uniformly throughout the particle. This type of reaction is illustrated in Fig. 1(a). The rate of reaction is dependent only upon the amount of plutonium available providing that the hydrogen availability is not limited. The first-order rate equation for this model is

$$W_t = W_m(1 - e^{-Kt}) \tag{1}$$

where W_t is the amount of hydrogen reacted at time t, W_m is the maximum amount of hydrogen that can react and K is the rate constant.

If hydrogen does not diffuse rapidly through the plutonium particles, but is restricted at either the hydrogen–product or the hydrogen–plutonium interface, the "phase-boundary" model may be valid. The reaction predicted by this model occurs at the gas–plutonium interface as illustrated in Fig. 1(b). In this case the reaction front moves toward the center of the particle.

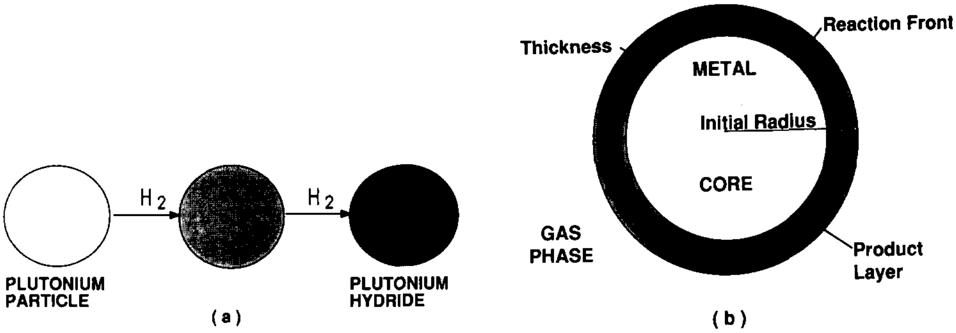

Fig. 1. (a) Progressive conversion model for plutonium powder hydriding; (b) phase-boundary model for plutonium powder hydriding.

The product hydride may be porous with no protective properties or it may be dense and present a diffusion barrier between the plutonium and hydrogen. If the product is protective the rate of reaction can be expressed by the Jander equation [10]

$$[1-(1-\alpha)^{1/3}]^2 = k_j t \tag{2}$$

where k_j is the rate constant, α is the fraction of plutonium reacted and t is the time elapsed.

If the product is porous, the phase-boundary reaction results in linear growth of the hydride layer. The rate equation then becomes

$$1-(1-\alpha)^{1/3} = k_l t \tag{3}$$

4. Results and discussion

4.1. *Coupon hydriding*

Hydriding of plutonium coupons was performed as a preparative step for the formation of plutonium powder. A typical coupon-hydriding run at 100 °C in 13.3 kPa of hydrogen is illustrated in Fig. 2. Initially, the reaction rate accelerated as hydride nucleation sites covered the surface and spallation of the hydride began. When the surface was fully covered by hydride, the rate of reaction became linear. The rate of reaction was proportional to the temperature and had a pressure dependence of $P^{1/2}$. The objective of the coupon-hydriding process was to provide a hydride powder and ultimately a plutonium powder with a minimum particle size. This objective could be realized by minimizing the hydriding rate [6]. Subsequent hydriding/dehydriding steps did not alter the particle size of the plutonium powder. Therefore all of the coupon hydriding was done at 25 °C and 0.07 kPa.

4.2. *Powder formation by hydride decomposition*

Kinetics for the decomposition of plutonium hydride were investigated earlier [11]. The dehydriding rate was influenced by temperature and also

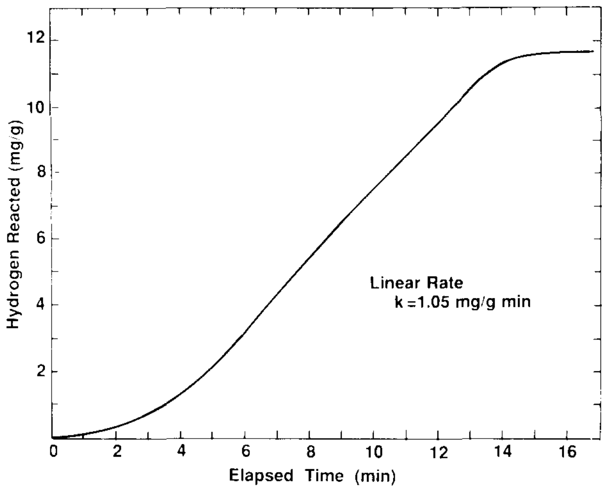

Fig. 2. Hydriding of a pre-nucleated plutonium coupon at 100 °C in 13.3 kPa of hydrogen.

by the residual hydrogen pressure in the system. The activation energy for hydride decomposition was 27 kcal mol^{-1} and the decomposition rate varied as a function of $P^{1/2}$. Combining both the temperature and pressure effects resulted in the following equation for the rate of decomposition of plutonium hydride:

$$k=(0.003\,69T'-1.349)P^{-1/2} \qquad (4)$$

(T', temperature in °C; $T'>366$ °C)

The surface area of the plutonium powder formed by hydride decomposition was measured using argon adsorption at −196 °C. The surface areas of the six samples varied from 0.18 to 0.28 $m^2\ g^{-1}$. Repeated hydriding/dehydriding cycles for any given sample did not alter the powder surface area.

4.3. Powder hydriding kinetics

4.3.1. Kinetic evaluation

Hydriding of plutonium powder is illustrated in Fig. 3 for a run at an initial temperature of 21 °C in 0.07 kPa hydrogen. This run is typical of all the experimental runs and illustrates both the kinetics of plutonium powder hydriding and the exothermic nature of this reaction. The reaction began immediately after the introduction of hydrogen regardless of the reaction conditions. The apparent inhibition shown in Fig. 3 was caused by a delay in hydrogen introduction and was taken into account in the data analysis. Plutonium hydriding is a very exothermic reaction and results in a significant increase in sample temperature during the hydriding run. This subject will be discussed further in the following section.

The rate of hydriding was evaluated using the kinetic models discussed earlier. The "progressive conversion" model, eqn. (1), was found to describe the total reaction very well as shown in Fig. 3. Equation (2) of the "phase-

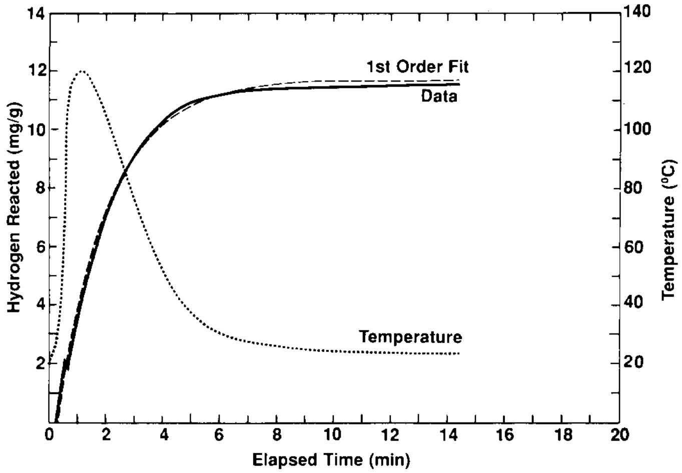

Fig. 3. Hydriding of plutonium powder at 21 °C in 0.07 kPa of hydrogen. The dashed line is the theoretical fit using the progressive conversion model.

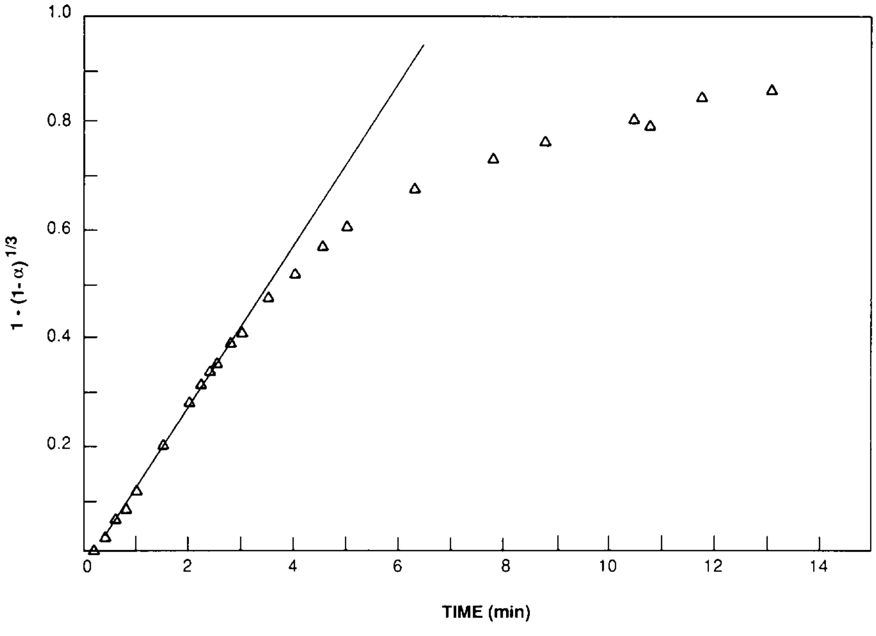

Fig. 4. Analysis of plutonium powder hydriding at 21 °C in 0.07 kPa of hydrogen using the phase-boundary model. The fit is valid only up to 3 min of reaction.

boundary" model did not fit the data for the first 50% of the reaction. This indicates that the hydride product layer presents no barrier to the reaction of hydrogen with plutonium. When the data were analyzed using eqn. (3), the initial interpretation showed that this model could not be used to define the entire plutonium hydriding reaction. A fit of the data, Fig. 4, was valid only for the initial stage of reaction. Further evaluation of this model revealed that it provided an accurate representation of the data to an H/Pu ratio of 2. This is precisely what would be expected from a reaction front moving through a particle. Subsequently, eqn. (3) was found to be valid in the two-phase region for all of the experiments, but it ceased to be valid when the reaction reached the dihydride solid-solution stage.

The equilibrium composition of the hydride formed varied with temperature and to a lesser degree with the hydrogen pressure. Figure 5 shows the equilibrium composition of the plutonium hydride as a function of temperature at 0.007, 0.07 and 26.5 kPa of hydrogen. Scatter in the data was due to terminating the runs before true equilibrium was reached. At low pressures (0.007 and 0.07 kPa) pressure had little effect on the hydride composition. Two runs at 26.6 kPa indicate that there is a pressure effect at higher pressures, but this was not really defined in this investigation.

Kinetic data from all of the experiments are summarized in Table 2. The surface areas of the powder samples were nearly identical and no surface area dependence could be determined. The reaction temperatures shown in this table are the average temperature values along with their standard error. The error in the temperatures gives a good indication of the variation in temperature during the reaction. The first-order rate constants reported were derived from both the progressive conversion model (eqn. (1)) and the phase boundary model (eqn. (3)).

4.3.2. *Effect of temperature on hydriding kinetics*

Data illustrated in Fig. 3 and tabulated in Table 2 point to the fact that these runs were not made under isothermal conditions. There was considerable

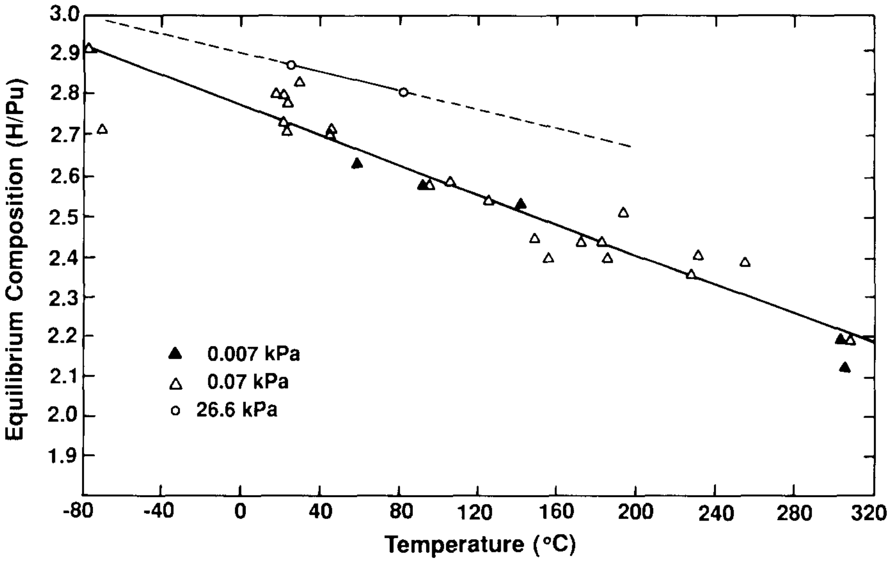

Fig. 5. The effect of pressure and temperature on the equilibrium composition of the plutonium hydride product.

TABLE 2

Hydriding kinetics for plutonium powder

Sample	Temperature (°C)	Pressure (kPa)	Eqn. (1) K (min^{-1})	Eqn. (3) k_l (min^{-1})	Surface (m^2 g^{-1})
1	47±20	0.07	0.38	0.11	0.25
	255±18	0.07	0.48	0.13	0.25
	56±23	0.07	0.51	0.15	0.25
	200±18	0.07	0.46	0.14	0.25
2	65±20	0.07	0.55	0.16	0.25
	127±18	0.07	0.49	0.14	0.25
	150±18	0.07	0.51	0.15	0.25
	257±16	0.07	0.50	0.14	0.25
	50±21	0.07	0.54	0.15	0.25
	324±14	0.07	0.50	0.13	0.25
	50±21	0.07	0.49	0.14	0.25
3	67±35	0.07	0.53	0.16	0.18
	276±32	0.07	0.67	0.13	0.18
4	128±23	0.07	0.53	0.11	0.23
	210±20	0.07	0.42	0.12	0.23
	−21±34	0.07	0.48	0.15	0.23
5	353±11	0.07	0.36	0.12	0.20
	149±16	0.07	0.37	0.12	0.20
	82±19	0.07	0.38	0.12	0.20
	197±16	0.07	0.41	0.12	0.20
	−41±20	0.07	0.47	0.15	0.20
6	250±14	0.07	0.41	0.12	0.28
	58±17	0.07	0.44	0.12	0.28
	119±31	26.5	1.79	0.60	0.28
	67±41	26.5	2.45	0.42	0.28
	177±16	0.07	0.39	0.12	0.28
	75±11	0.007	0.078	0.025	0.28
	154±7	0.007	0.052	0.017	0.28
	313±4	0.007	0.044	0.020	0.28
	201±6	0.007	0.046	0.017	0.28
	110±7	0.007	0.045	0.015	0.28
	37±7	0.007	0.038	0.014	0.28
	313±3	0.007	0.044	0.016	0.28

concern as the experiments were being conducted about evaluating the effect of temperature on the reaction kinetics. Earlier studies showed no temperature dependence for the hydriding of a plutonium alloy [6]. Therefore in this investigation a very wide range of temperature (about 400 °C) was selected in order to override the inaccuracies in temperature measurement and the non-isothermal nature of the reactions. A comparison of the reaction rates obtained from eqn. (1) with the average run temperature is shown for three pressures in Fig. 6. Within experimental error, all of the data indicate that the rate of plutonium hydriding is independent of the temperature. This supports the results observed for the hydriding of plutonium–1wt.% gallium reported earlier [6]. Activation energies calculated for the hydriding reaction in 0.007 and 0.07 kPa of hydrogen were -0.61 and -0.21 kJ mol^{-1} respectively. Near zero activation energies are unusual but have been reported for other systems. Akiba *et al.* [12] reported zero activation for the hydriding of two Mg–Ni alloys and this author [13] as well as Condon and Larson [14] reported the activation energy for the hydriding of uranium powder to be negative. A possible reason for the negative activation for uranium powder hydriding is discussed by Bloch and Mintz [15].

Figure 6 also shows a comparison between the hydriding rates for unalloyed plutonium powder and a plutonium–1wt.% gallium alloy powder in 0.07 and 26.5 kPa of hydrogen. The comparison at a pressure of 0.07 kPa shows that the rates are nearly identical over the temperature range -50 to 400 °C. This also appears to be true at a pressure of 26.5 kPa as shown by the two runs at 67 and 119 °C.

4.3.3. Effect of pressure on hydriding kinetics

The temperature and alloy independence of the hydriding reaction illustrated in Fig. 6 makes it possible to use all of the available data in evaluating the effect of pressure. Figure 7 illustrates the effect of pressure on hydriding in 0.007, 0.07 and 26.5 kPa of hydrogen at a temperature of about 70 °C. The effect of hydrogen pressure was evaluated using the relationship

$$K = aP^n \tag{5}$$

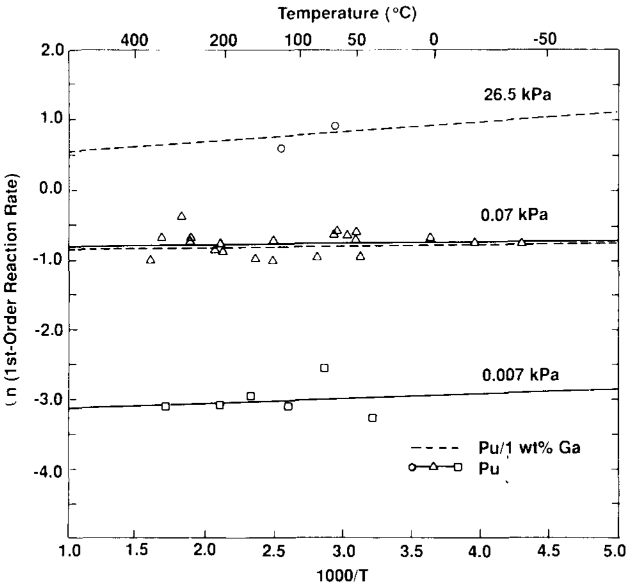

Fig. 6. The effect of temperature on the rate of hydriding of both plutonium and plutonium–1wt.% gallium alloy powder.

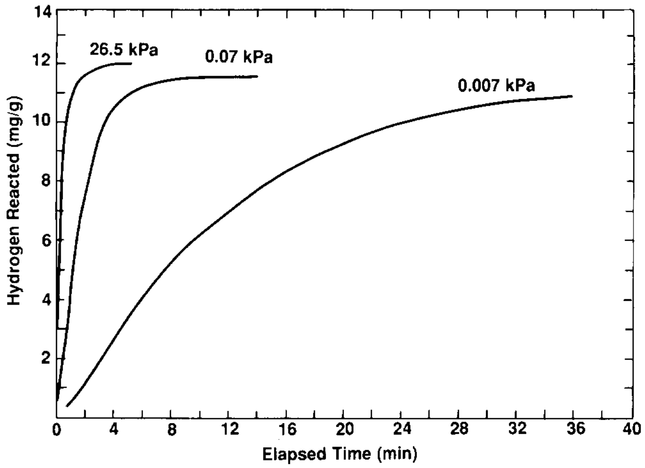

Fig. 7. Plutonium powder hydriding in 0.007, 0.07 and 26.5 kPa of hydrogen.

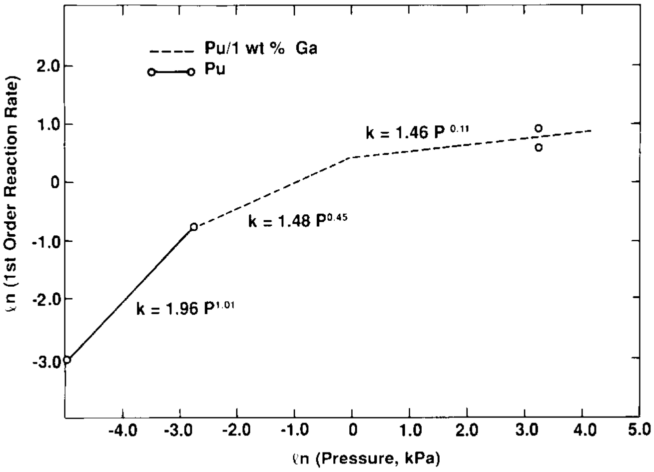

Fig. 8. Pressure dependence for the hydriding of plutonium and plutonium–1wt.% gallium alloy powder.

where K is the first-order rate constant from eqn. (1), P is the hydrogen pressure, and a and n are constants.

The effect of pressure over the pressure range 0.007 to 26.5 kPa is shown in Fig. 8. Data included in this figure are from ref. 6 as well as from the current investigation. The earlier study [6], using a plutonium–1wt.% gallium alloy powder, covered the hydrogen pressure range 0.07–68 kPa. These data showed two different pressure regions. Below 1 kPa the hydriding rate was proportional to $P^{1/2}$. Above 1 kPa the rate was nearly independent of hydrogen pressure. Current data include two runs at 26.5 kPa that are in good agreement with the earlier data in the pressure-independent region (see Fig. 8). The data point at 0.07 kPa represents an average of 23 runs and is also in good agreement with the previous data. These data fall in the lower end of the pressure range where hydriding rates are proportional to $P^{1/2}$. The single data point shown at 0.007 kPa is an average of 7 individual runs from the current study. Based on these data, a new pressure dependence for hydriding was determined in the pressure range 0.007–0.07 kPa. In this range, the rate of hydriding was proportional to P^1.

Understanding the pressure dependence of a reaction is important to understanding the reaction mechanism. In the case of plutonium hydriding, however, the pressure dependence becomes quite complex. Based on the earlier work [6] the hydrogen pressure dependence appeared to be fairly simple and was explained on the basis of a dissociative Langmuir adsorption. At pressures between 0.07 and 1 kPa hydriding was proportional to $P^{1/2}$ and controlled by the dissociative adsorption of hydrogen. Above 1 kPa hydriding was independent of pressure and the hydriding rate was reaction controlled. The present investigation verifies the earlier findings above 0.07 kPa; however, results at pressures below 0.07 kPa, where the rate is proportional to P^1, are new and require some additional explanations.

The process of plutonium hydriding consists of two steps, adsorption and solution (chemical reaction) with adsorption being the necessary first step in the hydriding reaction. The plutonium hydriding process may be described by a series of reactions similar to those used by Ehrlich [16] for metal oxidation:

$$\mathrm{H_2\ (gas)} \overset{K_1}{\longleftrightarrow} \mathrm{H_2\ (physisorbed)} \tag{6}$$

$$\mathrm{2Pu + H_2\ (physisorbed)} \overset{K_2}{\longleftrightarrow} \mathrm{2H\ (chemisorbed)} \tag{7}$$

$$\mathrm{H\ (chemisorbed)} \xrightarrow{k_3} \mathrm{H\ (hydridic)} \tag{8}$$

If equilibrium exists between chemisorbed and physically adsorbed hydrogen, the rate of hydriding k_{hyd} becomes

$$k_{\mathrm{hyd}} = \frac{k_3 K P^{1/2}}{1 + K P^{1/2}} \tag{9}$$

where $K = (K_1 K_2)^{1/2}$

At high hydrogen pressures $KP^{1/2} \gg 1$ and $k_{\mathrm{hyd}} = k_3$. Under these conditions the rate of hydriding is independent of the hydrogen pressure and adsorption is not a factor.

At low pressures where $KP^{1/2} \ll 1$

$$k_{\mathrm{hyd}} = k_3 K P^{1/2} \tag{10}$$

This type of behavior suggests that an adsorption equilibrium exists at the hydride–hydrogen interface and that the rate of hydriding is proportional to $P^{1/2}$ and controlled by the dissociative adsorption of hydrogen. This mechanism was observed in this study at 0.07 kPa and was described earlier by the Langmuir equation. Previous data [6] also indicate that the mechanism is at work in the pressure range 0.07–1 kPa.

At pressures below 0.07 kPa, in the present case between 0.007 and 0.07 kPa, the rate of hydriding was proportional to P^1. Since the temperatures involved were relatively high for hydrogen adsorption, it can be assumed that under such conditions the lifetime of physically adsorbed hydrogen is short. Therefore chemisorption (eqn. (7)) and thus the rate of hydriding, becomes controlled by the frequency of successful collisions between physically adsorbed hydrogen and the plutonium surface. The rate of physical adsorption may be written as

$$k_{\mathrm{phys}}=\frac{sP}{(2\pi mkT)^{1/2}} \tag{11}$$

where m is the hydrogen mass, k is the Boltzmann constant and s is the sticking probability for hydrogen. Adsorption in this case is directly proportional to pressure, which corresponds to the observed pressure dependence for plutonium powder hydriding between 0.007 and 0.07 kPa. A similar mechanism has been observed for the low pressure oxidation of iron [17] and niobium [18].

5. Conclusion

Reaction kinetics for the hydriding of plutonium powder were measured at temperatures between −41 and 350 °C and at hydrogen pressures between 0.007 and 26.5 kPa. Two models were used to evaluate the hydriding kinetics. The progressive conversion model, which assumes rapid diffusion of hydrogen, fits the data quite well in both the plutonium–plutonium hydride two-phase and the dihydride solid–solution regions. The phase-boundary model, which assumes a reaction front at the hydride–plutonium interface, was valid only in the two-phase region ($H/Pu<2.0$). The rate of hydriding was found to be independent of temperature. Furthermore, the rates were nearly identical with those previously measured for a plutonium–1wt.% gallium alloy.

Pressure effects on hydriding rates varied with pressure and fell into three categories: (1) pressure independent ($P>1$ kPa); (2) proportional to $P^{1/2}$ ($0.07<P<1$ kPa) and (3) proportional to P^1 ($P<0.07$ kPa). The observed cases of pressure dependence in categories (2) and (3) were explained by assuming that physical and chemical adsorption are the rate-controlling processes.

Acknowledgments

This work was performed under the auspices of the U.S. Department of Energy Contract DE-AC04-76DP03533.

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