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Plutonium hydride, sesquioxide and monoxide monohydride: pyrophoricity and catalysis of plutonium corrosion

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Abstract

Reaction rates of air and oxygen with cubic plutonium hydride (PuH_x, $1.9<x<3$), monoxide monohydride (PuOH), and Pu metal coated with these compounds are described, along with kinetic results for the $Pu+H_2$ reaction. Pyrophoric tendencies are not observed for PuOH, but exposure of PuH_x and PuH_x- (or PuOH-) coated Pu to air or O_2 at room temperature result in spontaneous reactions that consume both O_2 and N_2. These reactions and hydriding have zero or slightly negative activation energies and pressure-dependent rates. Pyrophoric reaction of PuH_x and PuH_x-catalyzed corrosion of Pu depend on thermal maintenance of catalytic Pu_2O_3 at the gas–solid interface and are prevented by formation of a protective PuO_2 layer at low temperatures and low O_2 pressures. The $Pu+H_2$ reaction is catalyzed by Pu_2O_3 and PuH_x is produced by the $Pu+H_2O$ reaction only at conditions where Pu_2O_3 formation is kinetically favored. Thermal ignition of Pu near 500°C is attributed to autoreduction of the PuO_2 surface to Pu_2O_3 at that temperature. At normal storage temperatures, formation of pyrophoric corrosion products is unlikely in open oxidant-rich systems, but surfaces that catalyze rapid Pu corrosion in air are formed during extended storage in closed systems.

Keywords: Corrosion; Actinides; Catalysis

1. Introduction

Chemical properties of plutonium are the source of several hazards cited in an assessment of vulnerabilities associated with handling and storage of metal and residues containing particles of metal [1]. Plutonium metal fines are classified as pyrophoric because they spontaneously ignite in the presence of oxygen if heated to 120–200°C. In contrast, large pieces of metal reportedly burn only when heated to red-hot temperatures. Plutonium hydride formed by facile reaction of metal with hydrogen from radiolysis of organic materials and from other sources is also categorized as pyrophoric and has additional capability for catalyzing oxidation. Chemical properties are described as complex and dependent on specific conditions.

Relevance of chemical behavior to handling and extended storage of plutonium is realized in the potential for thermal excursions, pressurization and failure of containment vessels, and transformation of massive metal into dispersible material forms [2]. A specific concern at Rocky Flats is that corrosion products formed by reaction of metal with moisture react upon exposure to air and act as thermal sources for ignition of residual plutonium metal [3]. A hypothetical product consisting of 5% PuH_2 formed by reaction of metal with water, 0.5% fine metal grains formed by rapid grain-boundary corrosion of the metal and 94.5% of the $PuO_{1.98}$ phase present at the lower boundary of substoichiometric dioxide is proposed. Although the existence of such mixtures is not confirmed experimentally, a potential for rapid exothermic reaction with air arises from the anticipated presence of hydride and mandates use of adequate procedures.

The complexity of plutonium ignition is suggested by diverse observations. Ignition points for unalloyed metal and alloy with a minimum thicknesses greater than 0.2 mm are in the 500±25°C range [4], not at ‘red heat’ as stated

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in the vulnerability report [1]. Particles with dimensions less than 0.1 mm ignite in air at 150–200°C, but instances are cited in which chips and lathe turnings spontaneously burned at room temperature [4]. Hydride-coated metal with thicknesses of 1–2 mm is consumed within minutes after exposure to air at room temperature [5]. Nitrogen and oxygen react indiscriminately at the 3.7:1 ratio of the elements in air to form PuN and Pu_2O_3 or an oxide–nitride solid solution of Pu(III) as hydride catalytically moves the reaction front into the metal. Hydride-catalyzed oxidation by O_2 at 3 bar is 10^{13} faster than corrosion of delta-phase gallium alloy in air at 25°C. The solid product is monolithic with a hydride core encased in a thick Pu_2O_3 shell. Contrary to earlier indications that cubic, α-phase Pu_2O_3 (hereafter identified as Pu_2O_3 or sesquioxide) protects against oxidation [6], these results suggest that Pu_2O_3 is highly reactive [7].

Other studies suggest that corrosion is promoted by Pu_2O_3, PuH_2, and other potentially pyrophoric and catalytic materials. Failure of small Pu particles to ignite in air below 150°C implies that metal fines are not inherently pyrophoric at room temperature [4], but reoxidation of the Pu_2O_3 layer formed by autoreduction of surface PuO_2 above 150°C [8] provides sufficient heat to increase the temperatures of high-surface-area (<0.1 mm thickness or radius) metal to the 500°C ignition point [7]. Plutonium monoxide monohydride (PuOH) is a potentially reactive compound formed by corrosion of Pu in liquid water at room temperature [9,10]. PuOH crystallizes in a fluorite-related structure with anionic sites in a Pu(III) lattice occupied by O^{2-} and H^-. However, the stoichiometric oxide hydride differs from the nonstoichiometric hydride, a cubic PuH_x solid solution ($1.9<x<3$) formed by accommodating anion vacancies or H^- interstitials in the fluorite structure [11]. Unlike the relatively unreactive hexagonal PuH_{3-y} phase obtained by reacting Pu with excess H_2 at elevated temperature and pressure [12,13], PuH_x forms at low temperatures and pressures and is considered highly reactive in air [14].

Perplexing observations made during reaction of hydride with oxygen are inconsistent with pyrophoric tendencies [15,16]. Reaction initiated immediately after exposure of PuH_x ($2.0<x<2.7$) to O_2 at 13.3 mbar (10 Torr) pressure and temperatures of 50–360°C, but ceased abruptly after 2 min (20% completion) at 50°C. Oxidation of PuH_x to PuO_2 was complete only after 1.5 h at 360°C. A negative activation energy (-9 kJ mol^{-1}) for the initial reaction implies that oxidation of PuH_x is not autothermic.

In this study, we examine the pyrophoric tendencies of PuH_x and PuOH, investigate the catalytic involvement of these hydridic compounds and Pu_2O_3 in plutonium corrosion, and identify properties and conditions that promote pyrophoric behavior. We also determine the temperature and pressure dependencies of Pu corrosion by hydrogen and by hydride-catalyzed reaction of metal with air. Results and data from literature sources are applied in describing pyrophoric tendencies of compounds and ignition of metal in air.

2. Experimental methods

Chemical and kinetic behavior of PuOH and of electrorefined Pu metal (major impurity: 200 ppm Am) and weapons-grade delta-phase gallium alloy with surface coatings of Pu_2O_3, PuOH, and PuH_x were investigated using PVT (pressure–volume–temperature) methods. A volume-calibrated stainless steel test system designed for high pressure and high vacuum operation consisted of a manifold, reactors (40–50 cm^3), and an auxiliary volume. Thermocouples and pressure transducers allowed for measurement of T and P in each volume. Tests were conducted with accurately weighed metal specimens (5–12 g) having thicknesses of 1–2 mm and known geometric areas. The specimen temperature was fixed by placing a He atmosphere in the reactor and heating with a resistance element or cooling with a coil containing a flow of refrigerated perfluorocarbon liquid before evacuation and addition of reactant gas. Gases were analyzed with a quadrupole mass spectrometer calibrated for ionization efficiency and fragmentation. Calibrations were made using gases with the highest available purity (Matheson) and selected mixtures by referencing measured spectra to that for N_2.

Desired compounds were formed on metal surfaces by chemical treatment of plutonium specimens at conditions known to yield those products. Characterization of prepared surfaces was precluded by the presence of highly reactive compounds and the inability to perform analyses without removing specimens from the controlled-atmosphere of the test system. The validity of surface analyses would be compromised by the likelihood of reaction with trace contaminants during handling. The potential for violent reaction with air and dispersal of plutonium created an unacceptable safety risk.

Reactions of unalloyed and alloyed Pu with H_2 were investigated in experiments with excess metal at conditions that produce PuH_x. Each metal specimen was exposed to a known amount of H_2 at 4 bar H_2 and a temperature of -20 to 300°C by expanding a measured quantity of gas from the auxiliary volume into the system, isolating the reactor, and determining by difference the amount delivered. Reactions of the oxide-coated specimens were sluggish below 150°C and hydriding rates reached maxima when metal surfaces were fully covered by PuH_x. In those cases, reaction was stopped by venting and evacuation after a rate maximum was reached. Kinetic measurements were made after active specimens were reexposed to H_2 at 4 bar. P–T data were measured as a function of time, t, until the residual pressure approached zero.

Kinetic data were also measured at temperatures below 150°C using oxide-coated specimens with surfaces that were chemically altered by heating in vacuum at 150–

200°C for 0.5 h. At those conditions, the PuO_2 layer formed on the metal during air exposure is reduced to cubic Pu_2O_3 by Pu [8]:

$$3PuO_2\ (s) + Pu\ (s) \rightarrow 4\ Pu_2O_3\ (s, cubic) \quad (1)$$

P–T–t data were measured after specimens were exposed to 4 bar H_2. The Pu_2O_3 layers had maximum thicknesses on the order of 5 μm as determined by that of the adherent PuO_2 layer existing on the metal in air at room temperature [7] and were apparently removed by spallation as PuH_x formed at the product–metal interface during the reaction.

A series of isothermal hydriding experiments were also made using large, high-surface-area metal specimens to sensitize the measurements. The test system consisted of a reactor fitted with a thermocouple, a low pressure (0.1–1.3 mbar) transducer and a H_2-calibrated flow meter. After an alloy sample had been activated with PuH_x, the temperature and flow rate of H_2 into the system were fixed. The H_2 pressure increased as gas accumulated in the system and became constant (steady state) when the rates of hydriding and flow of H_2 into the system were equal. Rates of reaction and the corresponding steady-state pressures were measured at 50°C and successively increasing and decreasing H_2 flow rates.

Samples of PuOH and PuOH-coated metal were prepared by total or partial reaction of alloy specimens submerged in 0.05 M NaCl solution [9,10]. The extent of reaction was monitored using PVT data to determine the amount of H_2 produced by the corrosion reaction:

$$Pu\ (s) + H_2O\ (l) \rightarrow PuOH\ (s) + 1/2H_2\ (g) \quad (2)$$

Occurrence of Eq. (2) was verified by agreement of the measured reaction rate (1.9±0.1 mg Pu cm^{-2} min^{-1}) with that (2.0 mg Pu cm^{-2} min^{-1}) predicted for 0.05 M chloride solution at near-neutral pH [17]. Formation of a more oxygen-rich phase by reaction of PuOH and corrosion of metal beyond about 50% were prevented by drying products in dynamic vacuum [18]. As in earlier PVT experiments with PuH_x and with PuH_x-coated Pu [5], reactivities of PuOH and PuOH-coated metal with air were investigated by rapid expansion of dry air from an auxiliary volume into evacuated reactors containing the test specimens. Initial pressures of the expanded air were 1.01 bar. Pressure and gas-phase temperature near the specimen were measured as a function of time and residual gases were analyzed by mass spectrometry.

Rates of reaction were derived from experimental P–T–t data using incremental changes in temperature-corrected reactant pressure during corresponding time periods or from the rates of gas flow into the reactor. Results for metal specimens are reported in units of Pu mass consumed per unit area of geometric surface per unit time. Reaction rates for powders are reported as mass of gas or Pu reacted per unit of true (BET) surface area per unit time.

3. Results and discussion

3.1. The general kinetic relationship

The rate, R, of a gas–solid reaction is described by a general expression that includes dependencies on temperature and the partial pressures $P1, P2, P3, \ldots$ of gaseous reactants 1, 2, 3, . . . :

$$R = k \exp(-E_a/R^*T)\ P1^{n1}P2^{n2}P3^{n3} \ldots \quad (3)$$

In addition to the proportionality constant (k), this equation includes an Arrhenius term defined by the activation energy (E_a), the gas constant (R^*), and temperature. Dependencies of R on concentrations of gaseous reactants are shown by the pressure exponents $n1, n2, n3, \ldots$.

3.2. Reaction of plutonium with hydrogen

As reported in earlier studies [14,19], corrosion of plutonium by hydrogen is rapid, but surprisingly insensitive to temperature. Definition of the chemical reaction is imprecise because of the variable stoichiometry of the hydriding reaction:

$$Pu\ (s) + x/2H_2\ (g) \rightarrow PuH_x\ (s) \quad (4)$$

Hydride nonstoichiometry and composition changes induced by hydrogen addition ($PuH_{x+\delta}$ formation) or removal ($PuH_{x-\delta}$ formation) are important in determining hydride reactivity. However, chemical reactions involving changes in composition of the nonstoichiometric hydride are difficult to measure and formulate. The PuH_x phase extends from about $PuH_{1.9}$ to near PuH_3 and δ may simultaneously vary from 0 to 1.1 depending on conditions. Equilibrium data for PuH_x indicate that the hydride composition at the gas–solid interface may vary from $PuH_{2.7}$ to $PuH_{2.3}$ at one bar H_2 pressure as sample temperature increases from 100 to 500°C, while the stoichiometry at the product–metal interface remains near $PuH_{1.95}$ over that range [11]. PuH_x reacts with H_2 at a rate comparable to that of the $Pu+H_2$ reaction [13] and high-composition hydride probably forms as particles spall and cool [14]. Therefore, neither hydride composition nor the amount of Pu reacted is precisely defined by PVT data at any point in time during the exothermic reaction. Rates for Eq. (4) are calculated assuming that the product is PuH_2. Reactions involving changes in hydride composition are written using PuH_2 to designate low-composition hydride ($PuH_{x-\delta}$) and PuH_x to designate high-composition hydride ($PuH_{x+\delta}$). Use of PuH_2 facilitates the calculation of rate and the formulation of balanced equations; it does not

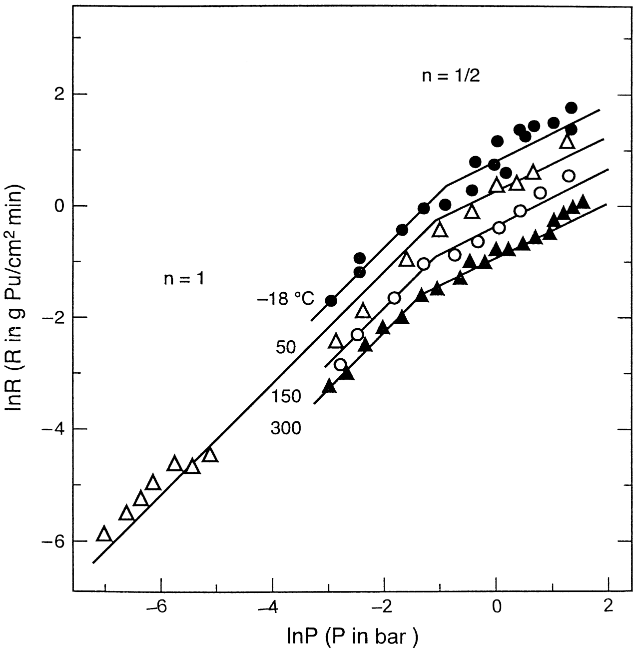

Fig. 1. Dependence of $\ln R$ on $\ln PH_2$ for reaction of Pu with H_2 at selected temperatures in the −20 to 350°C range. Data at H_2 pressures greater and less than 15 mbar ($\ln P = -4.2$) are from PVT and flow measurements, respectively.

mean that stoichiometric dihydride exists as a distinct phase apart from the PuH_x solid solution.

Rate data in Fig. 1 are from representative tests selected with wide temperature spacing in order to resolve individual data sets. Results for unalloyed and alloyed Pu at 0, 25, 75, 100, 200, and 250°C fall systematically within these data. As indicated by lines with ideal slopes, the $\ln R - \ln PH_2$ are accurately described by values of $n = 1$ at pressures below 0.27 bar ($\ln P = -1.3$) and by $n = 1/2$ at higher pressures. The $n = 1$ dependence is confirmed by agreement of PVT results with rates measured during constant-flow experiments at low pressures and 50°C. Insensitivity of the hydriding rate to temperature is suggested by appearance of linear $\ln R - \ln P$ relationships even though gas phase temperatures increased by more than 100° during the tests. Respective rates (2.48, 1.38, 0.78 and 0.43 g Pu cm^{-2} min^{-1}) at 1.01 bar H_2 pressure and −18, 50, 150, and 300°C define the Arrhenius relationship for the $Pu + H_2$ reaction at $250 < T < 575$ K:

$$\ln R\,(R \text{ in g Pu cm}^{-2}\text{ min}^{-1}\text{ at 1.01 bar H}_2) = -(2.19 \pm 0.11) + (805 \pm 39)/T \tag{5}$$

The apparent E_a for hydriding is −6.7 kJ mol^{-1} (−1.7 kcal mol^{-1}), a result consistent with dependence of the rate on the concentration of H_2 adsorbed at the gas–solid interface and with a progressively decrease in that concentration with increasing temperature at constant PH_2.

Hydriding rates at temperatures in the 250–575 K range and H_2 pressures in the 1 mbar to 4 bar range are defined by the general rate equation for the $Pu + H_2$ reaction:

$$R\,(\text{g Pu cm}^{-2}\text{ min}^{-1}) = 0.0567\exp(805/T)(3.75PH_2)^n \tag{6}$$

The reference H_2 pressure for this equation is the 0.27 bar transition point. Therefore, rates at pressures below this point are derived using $n = 1$ and those at higher PH_2 are calculated using $n = 1/2$. R at PH_2 values bracketing 0.27 bar give apparent pressure exponents between 0.5 and 1 and are consistent with measured n values of 0.6 [20] and 0.7 [21] for H_2 pressures in the transition region. The hydriding rate at 25°C and 1.01 bar H_2 is 1.65 g Pu cm^{-2} min^{-1}, a rate corresponding to advancement of the reaction front into the metal at 6 cm h^{-1}. This rate shows that the rates of H_2 dissociation at the gas–solid interface and of H transport through the PuH_x layer on the metal surface are unusually rapid.

Hydriding kinetics of Pu_2O_3-coated plutonium are indistinguishable from those observed after full activation of the metal by PuH_x. Maximum rates were observed immediately upon exposure of specimens to H_2 at temperatures below 150°C. This absence of sluggish behavior is consistent with facile formation of Pu_2O_3 on Pu surfaces in O_2-free atmospheres at these temperatures via Eq. (1) and implies that cubic Pu_2O_3 dissociates and transports hydrogen at rates equal to those of PuH_x.

Flow tests demonstrate that R of the $Pu + H_2$ reaction and PH_2 are coupled. The hydriding rate decreased as the H_2 pressure dropped during PVT experiments, but PH_2 was fixed at the rate of H_2 addition during constant-flow experiments. The hydriding rate is fixed by the H_2 pressure, or PH_2 is fixed by R.

As predicted by the Langmuir model, R is proportional to PH_2 to the first power at low pressures and is apparently controlled by the impingement rate of H_2 on the solid. In the higher-pressure regime defined by a square-root dependence on PH_2, behavior is consistent with dissociative adsorption of H_2 at the gas–solid interface. Although behavior parallels that for the $U + H_2$ reaction [19], R for U at the transition point from $n = 1$ to $n = 0.5 \pm 0.1$ is near 5 μbar H_2, a factor of 10^3 less than R for Pu. Saturation of the gas–solid interface at H_2 pressures above 2 bar during reaction is indicated for U by independence of R on PH_2 at high pressures, but similar behavior is not seen for Pu. A progressive increase in E_a with PH_2 over the $n = 1/2$ range and coincidence of E_a (29 kJ mol^{-1}) for hydriding in the $n = 0$ regime with that (30±5 kJ mol^{-1}) for hydrogen self-diffusion in UH_3 imply that R for the $U + H_2$ reaction is controlled by the combined effects of dissociative adsorption and H diffusion through the hydride surface layer in the 5 μbar to 2 bar range and solely by diffusion at higher pressures. A zero or slightly negative E_a in the $n = 1/2$ regime for the $Pu + H_2$ reaction implies that R is determined only by the concentration of dissociatively adsorbed hydrogen on the catalytic PuH_x surface at pressures up to 4 bar. Equivalence of the hydriding rates for Pu coated with PuH_x and with Pu_2O_3 suggests that a similar process occurs on the sesquioxide.

Comparison of the hydriding rates with those for powdered metal [22,23] show consistent kinetic behavior and define the relationship between geometric and true surface areas of massive Pu. Gravimetric measurements of the reaction between freshly prepared Pu powder (0.20 ± 0.05 m^2 g^{-1} BET area) and H_2 at −29 to 355°C show a near-zero (33 J mol^{-1}) E_a. Extent-time data for 30°C and 10.6 mbar H_2 pressure show complete reaction to $PuH_{2.63}$ after 3 min. The R (1.7 ± 0.4 mg Pu cm^{-2} min^{-1}) derived from the initial mass–t slope is 19±5-fold less than the geometric rate (32 mg Pu cm^{-2} min^{-1}) calculated for those conditions using Eq. (6). This result confirms that true surface areas are about 20 times greater than geometric values [24].

3.3. Reaction of PuOH-coated plutonium with air

Measurements of pressure and temperature after rapid exposure of PuOH-coated alloy to excess air at room temperature show that reaction was complete after 5–6 min. P–t and T–t data for the reaction [17] are indistinguishable from those obtained following exposure of PuH_x-coated metal to air [5] and show that rapid corrosion occurred after a relatively slow initial stage. Mass spectrometric data for residual gases (0.15 bar) show that the both O_2 and N_2 were consumed indiscriminately at the 3.7:1 ratio of the elements in air. H_2 was not detected as a gaseous product, implying that hydrogen was retained as PuH_x in the solid product.

The initial stage of reaction accounts for less than 5% of the total reaction and is characterized by acceleration of the reaction over a 0.5-min period. Analysis shows that $\ln R$ increased as a linear function of t consistent with formation of hydride via a first-order process [17]. Since PuH_x does not react readily with N_2 at temperatures below 250°C [12], the initial stage is attributed to oxidation of PuOH and heating of the oxide hydride above its 105°C decomposition point [9,10]. In the presence of Pu metal, reaction apparently proceeds with formation of Pu_2O_3 at the gas–solid interface and PuH_x at the product–metal interface:

$$3x\mathrm{PuOH}\,(s) + (3-x)\,\mathrm{Pu}\,(s) \rightarrow x\mathrm{Pu_2O_3}\,(s) + 3\mathrm{PuH}_x\,(s) \quad (7)$$

The product configuration corresponds to that of the highly reactive specimens obtained by reacting oxide-coated metal with small amounts of H_2 at 400°C [5].

The second stage is a catalyzed-corrosion reaction identical to the rapid second stage of reaction following air exposure of metal coated with PuH_x or with a Pu_2O_3–PuH_x double layer [5]. Hydrogen produced by rapid reaction of O_2 and N_2 with PuH_2 is retained by formation of PuH_x and subsequent reaction with metal to reform PuH_2:

$$x\mathrm{PuH_2}\,(s) + 3(x-2)/4\mathrm{O_2}\,(g) \rightarrow (x-2)/2\mathrm{Pu_2O_3} + 2\mathrm{PuH}_x\,(s) \quad (8)$$

$$x\mathrm{PuH_2}\,(s) + (x-2)/2\mathrm{N_2}\,(g) \rightarrow (x-2)\mathrm{PuN} + 2\mathrm{PuH}_x\,(s) \quad (9)$$

$$\underline{4\mathrm{PuH}_x\,(s) + 2(x-2)\mathrm{Pu}\,(s) \rightarrow 2x\mathrm{PuH_2}\,(s)} \quad (10)$$

$$2\mathrm{Pu}\,(s) + 3/4\mathrm{O_2}\,(g) + 1/2\mathrm{N_2}\,(g) \rightarrow 1/2\mathrm{Pu_2O_3}\,(s) + \mathrm{PuN} \quad (11)$$

As noted in Section 3.2, low- and high-composition hydrides are indicated by PuH_2 and PuH_x, respectively. Eq. (11) results from a catalytic cycle in which hydride reacts with O_2 to form the Pu_2O_3 catalyst that dissociatively adsorbs both O_2 and N_2. PuH_x is also a catalytic intermediate for forming PuN from metal [25]. Product stoichiometry is determined by the concentrations of O_2 and N_2 in air and the net reaction consumes 1.86 mol of Pu per mol of air. This factor and the mol of metal show that the amount of gas consumed during reaction accounts for 99% of the Pu as Pu_2O_3, PuN, and PuH_x (x near 3) and demonstrates that PuO_2 is not formed.

Dependence of the corrosion rate on air pressure (P_a) is defined by the $\ln R - \ln P_a$ results for 0.2–0.7 bar range in Fig. 2. The idealized slope of the line for $n=2$ is in excellent agreement with the least-squares value of 1.995 ± 0.008. This result and observation of a second-order pressure dependence for hydride-catalyzed reaction at 2–3 bar air pressure [5] imply that the same corrosion rate is described by this rate relationship over a wide range of air pressure. The previously reported value of $n=3$ for pressures less than 3 bar [5] is not observed and apparently resulted from inadequate correction for thermal gradients in the PVT system.

A zero activation energy for the reaction is implied by the precise linearity of data in Fig. 2, even though the gas-phase temperature varied from 25 to 175°C during the measurement. A much larger variation in specimen temperature undoubtedly occurred and may have approached several hundred degrees [5]. In the absence of a temperature dependence, R depends only on air pressure and permits evaluation of the isobaric rate constant for each point in Fig. 2. Calculation of the average k for all data points assuming $E_a=0$ and $P_a=1$ bar gives 1.72 ± 0.07 g Pu cm^{-2} min^{-1} bar^{-2} and leads to the general rate equation for hydride-catalyzed corrosion of Pu in air:

$$R\,(\mathrm{g\ Pu\ cm^{-2}\ min^{-1}}) = 1.72P_a^2 \quad (12)$$

Fortuitously, the rate of corrosion in 1.01 bar air coincides with that (1.65 g Pu cm^{-2} min^{-1}) for the $Pu+H_2$ reaction at 1.01 bar H_2 and also advances into the metal at a rate of 6 cm h^{-1}.

Results of this study and the extremely rapid reaction between O_2 and metal coated with a Pu_2O_3–PuH_x double

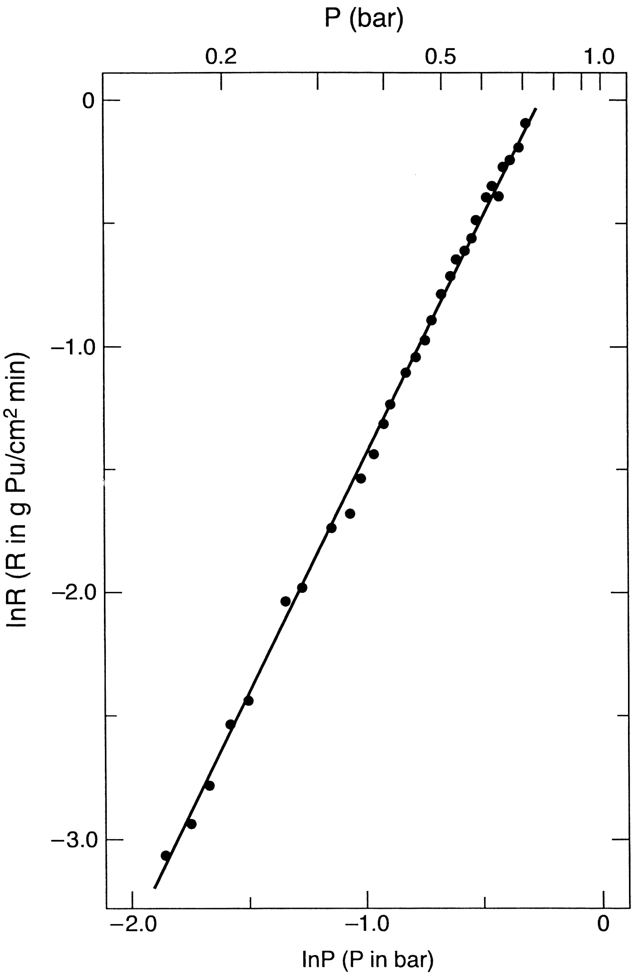

Fig. 2. Dependence of ln R on ln P_a after exposure of PuOH-coated delta phase alloy to air at 25°C and 1.01 bar.

layer [5] suggest that plutonium sesquioxide plays an important role in promoting corrosion. Products obtained in the earlier work had a PuH_x core encased in a thick shell of Pu_2O_3, implying that oxygen is dissociatively adsorbed at the sesquioxide surface and transported to the oxide–hydride interface. During catalyzed reaction of air, a product layer of Pu_2O_3 and PuN or an oxide nitride solid solution is apparently responsible for dissociative adsorption and transport of both oxygen and nitrogen. Although cracks and fissures in the product layer may provide direct access of O_2 and N_2 to the hydride layer, that possibility seems unlikely because exposure of PuH_x-coated Pu to air is followed by a relatively sluggish step like that observed for PuOH-coated metal [5]. Rapid initial reaction with air occurs only if a Pu_2O_3 layer preexists on the hydride surface.

A qualitative understanding of hydride-catalyzed corrosion is derived from known chemistry of participating materials. Whereas reaction of Pu metal with H_2 is rapid even at room temperature and reaction of Pu with O_2 proceeds at a slow rate at 25°C, direct reaction of Pu with N_2 is not observed at low temperatures and is less than 80% complete after 17 h at 1000°C [25]. However, O_2 readily reacts with PuH_x at room temperature and PuN is obtained by reacting N_2 with PuH_x at 300–400°C. During catalyzed reaction of air, oxygen and nitrogen are dissociatively adsorbed and transported to the product–hydride interface where they readily react with PuH_2 according to Eqs. (8) and (9). Nitriding is driven by the heat of oxidation. Product hydrogen is accommodated in the hydride lattice as higher-stoichiometry PuH_x and rapidly transported to the hydride–metal interface where PuH_2 is reformed at a rate comparable to that for hydriding at 1 bar H_2.

3.4. Reaction of PuOH with air

Results suggest that dry monoxide monohydride is not pyrophoric upon rapid exposure to air at 1.01 bar and 25°C. PVT measurements are inconclusive because reaction with O_2 to form Pu_2O_3 and H_2 is accompanied by a pressure increase and formation of PuO_2 and H_2 occurs without pressure change. Negligible reaction is indicated by failure to detect either a thermal excursion during the test or H_2 in the reactor atmosphere after its completion.

3.5. Reaction of PuH_x with air and oxygen

Earlier PVT studies [5] show that rapid exposure of PuH_x to air at 1.01 bar 25°C is accompanied by a pressure increase and a substantial thermal excursion during a 0.5-min period after addition of the gas. Analysis of residual gas in the reactor shows that O_2 was depleted and that H_2 was the major gaseous species. The primary reactant was N_2, a species that on average was consumed in a 1.6:1 molar ratio relative to O_2. Mass–balance calculations show that 5–20% of the PuH_x reacted with formation of 3–15% PuN and 2–5% Pu_2O_3. Reaction would probably have continued if additional oxygen in the auxiliary volume had been able to enter the reactor.

Incomplete reaction of hydride was also observed during microbalance studies in which PuH_x was exposed to excess O_2 at 13.3 mbar and temperatures of 50–360°C [15,16]. High-surface-area (0.20 ± 0.05 m^2 g^{-1}) PuH_x ($2.0<x<2.7$) specimens were prepared by repeated hydriding–dehydriding cycles and thermal treatment to adjust the final stoichiometry. Mass–time data (Fig. 3) measured following exposure of freshly prepared $PuH_{2.7}$ to H_2 at 50°C show that reaction initiated immediately, advanced at a linear (constant) rate until the extent of reaction reached 7 mg O g^{-1} PuH_x, and continued at a gradually decreasing rate until it slowed abruptly near 25 mg O g^{-1} PuH_x (20% transformation to PuO_2). Similar data for reaction of $PuH_{2.0}$ at 360°C [15] show an initial linear gain of 30 mg O g^{-1} PuH_x over an 8-min period and a progressively decreasing extent of reaction until a second linear mass–

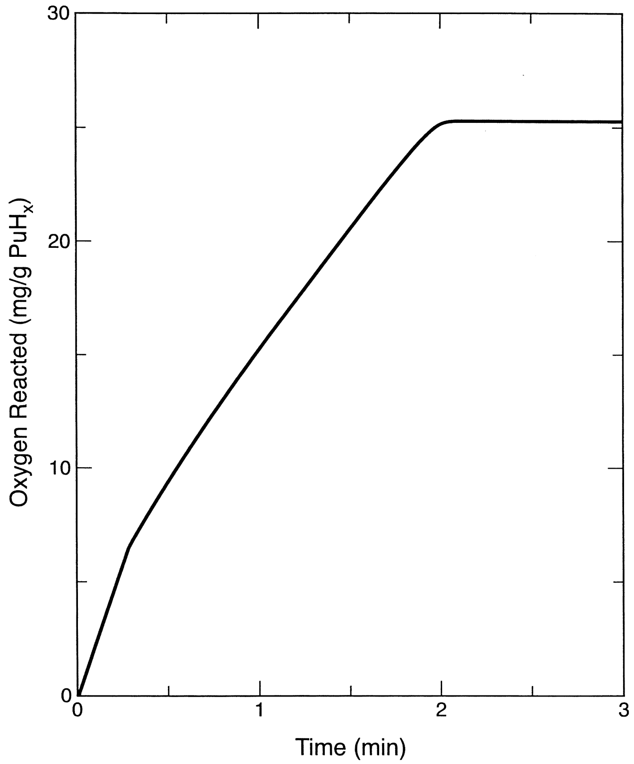

Fig. 3. Mass–time data for reaction of $PuH_{2.7}$ with O_2 at 50°C and 13.3 mbar. Data are from Refs. [15,16].

time regime was entered after 70 min. Formation of PuO_2 was about 95% complete after 90 min. Results in Fig. 4 show that stepwise mass gains occurred at successively higher temperatures after an initial exposure of $PuH_{2.7}$ to O_2 at 50°C. During graphically omitted time intervals between tests, the microbalance system was evacuated and the sample temperature was increased before O_2 was reintroduced. Behavior at each temperature is similar to that for exposure of PuH_x to O_2 with a relatively rapid linear initial reaction and a slow linear terminal reaction.

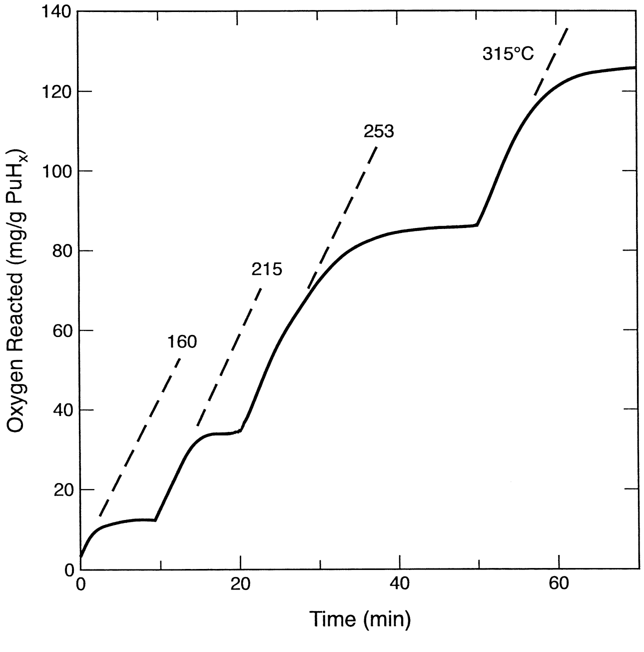

Fig. 4. Composite mass–time data for reaction of PuH_x with O_2 at 13.3 mbar and progressively increasing constant temperatures. Reaction rates are defined by dashed lines indicating initial slopes. Data are from Ref. [16].

Prior analysis of the kinetic results concluded that oxidation of PuH_x is a two-stage process in which the mass–time isotherms follow first-order kinetics during an initial reaction and linear (constant rate) kinetics during a secondary (terminal) reaction [15,16]. First-order rate constants for initial oxidation give $E_a = -9$ kJ mol^{-1}, suggesting that the reaction has zero activation energy. The secondary reaction has an activation energy of 42 kJ mol^{-1} and was identified as slow oxidation of hydride by diffusion of oxygen through a protective PuO_2 film on the hydride surface. Although the surface oxide was not identified by XRD, mass data in Fig. 4 show extent of reaction in excess of that for Pu_2O_3 (88 mg O g^{-1} of PuH_x). Conformity of secondary rates to a single Arrhenius relationship implies that dioxide was present during the terminal period of all tests. Since the hydride was coated by oxide during both the rapid initial and slow secondary stages of oxidation, different oxides were apparently present during those stages.

Reassessment of data for the $PuH_2 + O_2$ reaction [15,16] focuses on initial oxidation and the apparent existence of two distinct steps instead of a single first-order process prior to secondary reaction. As seen in Figs. 3 and 4, the linear mass–time step is followed by a non-linear step in which the rate decreases gradually. Oxidation rates defined by the initial linear segments at several temperatures (Table 1) give an E_a of -7.8 kJ mol^{-1}. Data for PuH_x coated with oxide prior to testing give an E_a of -2.3 kJ mol^{-1}. These results confirm that the initial step has zero activation energy, and that unlike the protective PuO_2 layer present during secondary reaction, the oxide present during initial reaction has little effect on the oxidation rate of PuH_x. Behavior is similar to Pu_2O_3-catalyzed corrosion of Pu by H_2, O_2, and air and suggests that sesquioxide is present during the initial reaction.

Table 1
Initial rates for oxidation of PuH_x by O_2 at 13.3 mbar pressure and 50–360°C[a]

Solid reactant	Temperature (°C)	R^b (μg Pu cm^{-2} min^{-1})
$PuH_{2.7}$	50	88
Oxide-coated PuH_x	160±1	36
Oxide-coated PuH_x	215±2	34
Oxide-coated PuH_x	253±10	32
Oxide-coated PuH_x	315±2	31
$PuH_{2.0}$	360	21

[a] Data are derived from mass–time curves presented in Refs. [15,16].

[b] Rates are calculated from the initial slope of the mass–time curve and a surface area of 0.2 m^2 g^{-1}.

Although the oxide present on the hydride at the beginning of each test was not identified, free energy data [26] show that reduction of PuO_2 by PuH_x is favorable. Pu_2O_3 undoubtedly formed as the sample was heated in vacuum prior to each test:

$$3PuO_2\,(s) + (1 + 2y)PuH_2\,(s) \rightarrow 2Pu_2O_3\,(s) + 2yPuH_x\,(s) \quad (13)$$

The y coefficient accounts for the molar ratio of hydride to dioxide in the reacting mixture and determines the stoichiometry of the hydride product: $x = (2y + 1)/y$. The value of x remains near 2 if y is large, but increases sharply for small y. Favorable kinetics of reduction are expected because oxygen is readily transported by the Pu_2O_3 product separating the reactants. Formation of PuH_x shows that hydride behaves like Pu in accommodating product hydrogen, but the capacity is significantly lower.

Correspondence of the initial $PuH_x + O_2$ reaction and the PuH_x-catalyzed $Pu + O_2$ reaction is suggested by comparing results in Table 1 with the geometric rate of metal corrosion (78 g Pu cm^{-2} min^{-1}) measured at a median O_2 pressure of 3.2 bar and temperatures in excess of 1000°C [5]. This rate is adjusted to the BET-equivalent value (3.9 g Pu cm^{-2} min^{-1}) using the factor of 20 relating geometric and true areas. Comparison with the median initial rate (55 μg Pu cm^{-2} min^{-1}) at 13.3 mbar O_2 is possible because both processes are temperature independent. The pressure coefficient defined by $\Delta \ln R/\Delta \ln P$ ratio is 2.04, a value close to that observed for PuH_x-catalyzed corrosion of Pu by air. This result defines the general rate relationship for temperature-independent initial oxidation of PuH_x powder by O_2:

$$R\,(\text{g PuH}_x\,\text{cm}^{-2}\,\text{min}^{-1}) = 0.37(PO_2)^2 \quad \text{(BET area)} \quad (14)$$

The corresponding general equation for PuH_x-catalyzed oxidation of massive Pu by O_2 is derived by inclusion of the areal factor:

$$R\,(\text{g Pu cm}^{-2}\,\text{min}^{-1}) = 7.4(PO_2)^2 \quad \text{(geometric area)} \quad (15)$$

Correspondence of rates for unalloyed and alloyed metal during hydriding and PuH_x-catalyzed corrosion [5] implies that Eq. (15) is independent of alloying.

Insight into the reactions of PuH_x and PuH_x-coated Pu with air is gained by use of Eq. (15) in deriving the general rate relationship for PuH_x-catalyzed corrosion of Pu in air. The squared dependence of R on air pressure (Eq. (12)) is assumed to arise from the partial pressure of O_2. The pressure exponent for N_2 is assumed to be zero. If reaction of nitrogen is driven by the thermal effect of O_2 reaction, the molar ratio of Pu consumed by N_2 to that consumed by O_2 during indiscriminate corrosion of metal by air (5.57:1) is determined by the mole percentages of the elements in air and the stoichiometry of Eq. (11). Inclusion of this factor and substitution of $PO_2 = 0.21P_a$ in Eq. (15) leads to a predicted general rate equation for corrosion of massive Pu in air:

$$R\,(\text{g Pu cm}^{-2}\,\text{min}^{-1}) = 1.8P_a^2 \quad (16)$$

The predicted rate at 1 bar air (1.8 g Pu cm^{-2} min^{-1}) is in excellent agreement with the experimental value of 1.72±0.07 g Pu cm^{-2} min^{-1}. These results imply that the same kinetic processes occur during initial reaction of PuH_x with air and PuH_x-catalyzed corrosion of Pu by air and that their rates are determined solely by the O_2 partial pressure.

The second step of the initial $PuH_x + O_2$ reaction is attributed to progressive transformation of the catalytic Pu_2O_3 layer on the hydride to protective PuO_2. The rate of this process is determined by the competing rates of PuO_2 reduction by PuH_2 (Eq. (13)) and Pu_2O_3 oxidation by O_2:

$$Pu_2O_3\,(s) + 1/2O_2\,(g) \rightarrow 2PuO_2\,(s) \quad (17)$$

Eq. (14) shows that the rate of initial reaction is independent of temperature, but as discussed below, reduction of PuO_2 to Pu_2O_3 is increasingly favored at the high temperatures generated by rapid reaction at high O_2 partial pressures. Formation of PuO_2 is kinetically favored by low temperature and low O_2 pressure.

Entry into the slow secondary stage of oxidation and ultimate formation of a protective PuO_2 layer is apparently initiated by production of H_2. Hydrogen formed during initial oxidation is accommodated primarily by increasing x of the PuH_x cores inside reacting hydride particles, but a small amount was present as H_2 at the equilibrium pressure (P_eH_2) defined by T and x of the PuH_x solid solution [11,27]. During isothermal oxidation measurements [15,16], the oxidation rate was not detectable altered as long as P_eH_2 was much less than the 13.3 mbar pressure of O_2. However, the bed of reacting hydride powder became filled with H_2 as x increased and P_eH_2 approached 13 mbar. The accompanying decrease in PO_2 within the bed slowed the rate of heat generation and resulted in progressive transformation of the Pu_2O_3 layer to PuO_2.

Involvement of H_2 in terminating rapid initial reaction is supported by extent-of-reaction data for $PuH_{2.0}$ at 360°C [15] and for $PuH_{2.7}$ at 50°C (Fig. 3) [16]. Deviation from linear behavior occurred when the respective x values of the PuH_x product reached 2.25 and 2.77. Extents of reaction during the linear step were small and temperatures remained essentially constant during initial reaction. Equilibrium data for PuH_x show that the x values at $P_eH_2 = 13$ mbar H_2 are 2.24 and 2.78 for 360 and 50°C, respectively [27].

Formation of PuO_2 on the PuH_x surface at low O_2 pressure is counterintuitive, but consistent with behavior of oxide on Pu metal. Since Pu_2O_3 coexists in equilibrium with Pu at all temperatures [28], appearance of PuO_2 as the only detectable oxide on the metal in air at 25°C is also counterintuitive and shows that formation of surface oxide is controlled by kinetics, not thermodynamics [9]. Extensive transformation of the dioxide layer to Pu_2O_3 during oxidation at 300°C [29] suggests that the $Pu + PuO_2$ reaction has a high E_a and increasingly competes with Eq. (17) at elevated temperatures. Penetration of the outer PuO_2 layer by 35 keV radiation during diffraction analysis of the product implies a maximum dioxide thickness of 0.1 μm and more than 90% transformation of the 10–15-μm thick oxide layer to Pu_2O_3. The rate of PuH_x oxidation is driven by high O_2 pressure and the accompanying heat generation promotes Pu_2O_3 formation. At low O_2 pressures, PuO_2 formation is favored because the rate of heat generation is slow and the rate of Eq. (17) exceeds that of Eq. (13).

As implied by the presence of Pu_2O_3 during rapid reaction of PuH_x with air and hydride-catalyzed corrosion of metal [5], PuH_x reacts rapidly with air only if sesquioxide is present at the gas–solid interface. The Pu_2O_3 surface participates with the underlying PuH_x in catalyzing corrosion. Whereas PuH_x promotes PuN formation and transports hydrogen at a surprisingly rapid rate, Pu_2O_3 dissociates and transports oxygen and nitrogen with equal facility. In contrast, oxidation of PuH_x is slowed by formation of PuO_2 [16].

4. Pyrophoricity and ignition of plutonium metal and compounds

4.1. Pyrophoricity of plutonium compounds

Pyrophoric behavior of reactive materials is predicated on favorable thermodynamics, but is controlled by kinetics. Free energies for reactions of PuH_2, Pu_2O_3, and PuOH with constituents of air are highly negative. Products and corresponding enthalpies of reaction are given in Table 2 with qualitative assessments of reactivity suggested by experimental observation. In addition to the effects of specific surface area, heat transfer, and oxygen concentration [4], important factors contributing to pyrophoric behavior include the ability the reacting solid to dissociatively adsorb and transport reactant and to accommodate additional anions in the existing structure.

The structures of all reactants and products in Table 2 have metal ions in fcc lattices. In the CaF_2-type structures of PuH_2 and PuO_2, tetrahedral sites in the cation lattice are fully occupied. The Mn_2O_3-type structure of Pu_2O_3 is derived from PuO_2 by removing 25% of the anions and reducing cations to Pu(III). Superstoichiometric PuH_x ($2 < x < 3$) is derived by filling octahedral sites in PuH_2, a metallic phase with Pu(III) on cation sites, H^- on anion sites, and one conduction electron per formula unit [11,19]. Electrical conductivity decreases with increasing x as conduction electrons are bound as hydride ions. The PuOH structure is derived by equal filling of tetrahedral sites in a Pu(III) lattice with O^{2-} and H^- in a 1:1 ratio. In the NaCl-type structure of PuN, tetrahedral sites of the fcc Pu(III) lattice are vacant and octahedral sites are occupied by N^{3-}. Rapid and continuing reaction of these solids with gases at room temperature depends on transport and accommodation of reactant anions within a stationary fcc metal lattice.

Plutonium hydride is classified as pyrophoric because the reaction is spontaneous and self-sustaining. As shown by experimental data, reaction of PuH_x with air initiates at room temperature and occurs with near-zero activation energy, an indication that Pu_2O_3 (or oxide nitride) on the hydride surface catalyzes dissociation of O_2 and N_2. Hydrogen formed by reactions of O_2 and N_2 is rapidly transported from the product–hydride interface into the bulk hydride and is accommodated as H^- in the hydride structure. Based on an average hydride thickness of 5 μm and the hydriding rate measured at 25°C and 1 bar H_2, the apparent coefficient for diffusion of hydrogen in PuH_x (10^{-3} cm^2 s^{-1}) far exceeds the value (10^{-11} cm^2 s^{-1}) derived for UH_3 from the lattice parameter and the hydrogen correlation time at room temperature [30]. The result for PuH_x is supported by proton NMR data indicating that diffusion is too fast for measurements at room temperature and that a rigid hydride lattice exists only at temperatures below −80°C [31]. Behavior is consistent with superionic conduction in PuH_x above this temperature [32]. Facile migration and accommodation of product hydrogen in the hydride promotes rapid initial reaction by preventing immediate accumulation of H_2 product at the gas–solid interface.

Accumulation of an oxygen-depleted nitrogen layer at the air–solid interface is precluded by reaction of N_2.

Table 2
Selected properties of plutonium compounds with potential for pyrophoric behavior

Compound	Reaction products formed in air	$\Delta H°$ of reaction with air[a] (kJ mol^{-1} Pu)	Qualitative pyrophoricity assessment
PuH_2	Pu_2O_3, PuN, PuH_x[b]	−293[c]	Pyrophoric
Pu_2O_3	PuO_2, residual N_2	−225	Highly reactive
PuOH	Pu_2O_3, H_2, residual N_2	−197	Potentially reactive

[a] Thermodynamic data are from Refs. [18,26].

[b] H_2 is produced as temperature and x of the PuH_x product increase.

[c] The enthalpy describes indiscriminate reaction of O_2 and N_2 with PuH_2 and reaches a minimum value of −234 kJ mol^{-1} Pu as x of the PuH_x product increases.

Nitriding is promoted by the heat of oxidation and apparently depends on the presence of catalytic Pu_2O_3 for rapid dissociation and transport of nitrogen. A sufficiently high O_2 pressure is needed to attain and maintain the temperature required for forming Pu_2O_3 and driving the $PuH_x + N_2$ reaction. Adequate heat is produced upon rapid exposure to air and reaction is not slowed by accumulation of residual N_2 at the surface. N_2 and O_2 react at the temperature-independent rate until the hydride composition approaches PuH_3 and the equilibrium H_2 pressure becomes sufficiently high to throttle reaction. In some cases, pyrophoric reaction apparently continues as product hydrogen burns at the solid surface.

Plutonium sesquioxide is classified as highly reactive because the extent of the $Pu_2O_3 + O_2$ reaction is limited. Dissociative adsorption of O_2 by Pu_2O_3, rapid transport of oxygen in the sesquioxide, and facile accommodation of reactant in vacant lattice sites are features that closely parallel those of PuH_x. Although the heat spike produced upon exposure to air is sufficient to ignite small metal particles [7], thermal effects are limited by the capacity of the Pu_2O_3 lattice for additional oxygen. Rapid oxidation is further throttled by accumulation of an oxygen-depleted N_2 layer at the gas–solid interface and by inherent formation of protective PuO_2.

Although plutonium monoxide monohydride is a hydridic compound with potential for pyrophoric behavior, experimental results indicate that PuOH is rather unreactive. Oxygen most likely interacts with PuOH at room temperature via a metathetic redox reaction in which O_2 and $2H^-$ are replaced by O^{2-} and H_2. Oxidation is hindered because movement of product hydrogen out of the solid and release of H_2 blocks transport pathways for O_2. Although vacant interstitial sites are present in the lattice, additional anions cannot be accommodated unless Pu(III) is oxidized to Pu(IV) as in the $Pu_2O_3 + O_2$ reaction. The initial reaction apparently generates insufficient heat for decomposition of oxide hydride into a more reactive chemical state [9,10] and spontaneous reaction is not observed at 25°C.

4.2. Ignition of plutonium metal

As noted in the introduction, controlled experiments show that plutonium particles with dimensions less than 0.1 mm ignite in air when heated to 150–200°C in air [7]. Specimens of Pu fines (50–100 μm size) prepared by filing massive metal and sieving the product in dried (200–700 ppm H_2O) air ignited upon heating to 175–200°C in flowing air [33]. Preparation of specimens by this procedure is possible only if oxide-free Pu particles do not spontaneously ignite in air at 25°C. Therefore, reports of spontaneous ignition involving both finely divided [4] and massive [2,5] metal at room temperature suggest that self-sustained reaction is initiated by reactive materials other than Pu.

Arrhenius results in Fig. 5 indicate that plutonium ignition is driven by both thermal and catalytic processes. As detailed in the caption, curves 1–9 define temperature-dependent corrosion rates for unalloyed and alloyed plutonium in humid and dry air at 25–3500°C [5]. Effects of alloying and moisture are absent above 400°C and thermally initiated oxidation is self-sustaining beyond 500°C, a temperature consistent with the ignition-point range of 500±25°C [7]. Rates of self-sustained oxidation in static air and in dynamic air during free fall of ignited Pu droplets are shown by curves 8 and 9, respectively. Oxidation in static air is temperature-independent because a nitrogen-rich boundary layer formed by depletion of oxygen at the gas–solid interface limits access of O_2 to the surface.

Temperature-independent rates indicated by curves 10–12 in Fig. 5 describe catalyzed corrosion reactions of plutonium. The PuH_x- or Pu_2O_3-catalyzed $Pu + H_2$ reaction initiates at 25°C. As shown by curve 11 for 1.0 bar H_2, hydriding of alloyed and unalloyed plutonium proceeds at an essentially constant rate until equilibrium in the metal–hydride system is reached near 885°C [34].

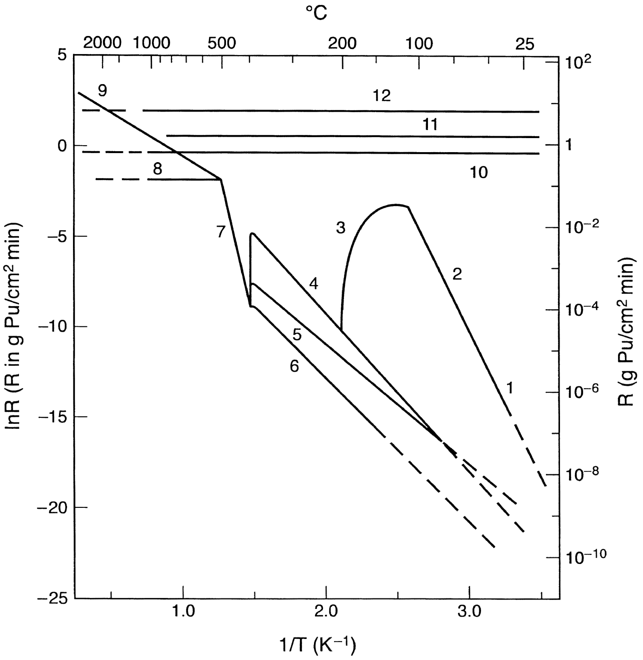

Fig. 5. Arrhenius results for corrosion of alloyed Pu and delta-phase alloy in different gaseous atmospheres. Curves 1–9 for oxidation in dry or moist air at 1.01 bar are from Ref. [5]. Curves 1–4 are for unalloyed metal; curves 5 and 6 are for alloy, and remaining data apply to both metallurgical forms. (1) Oxidation in H_2O-saturated air. (2) Oxidation in air with PH_2O at 0.21 bar. (3) Thermally-induced decrease at 110–200°C. (4) Oxidation in dry (<0.5 ppm H_2O) air below 200°C and dry or moist air above 200°C. (5) Oxidation in moist air. (6) Oxidation in dry air. (7) Oxidation in dry or moist air. (8) Oxidation of ignited Pu in static air. (9) Oxidation of ignited Pu in dynamic air. (10) PuH_x-catalyzed corrosion by O_2 and N_2 in air at 0.6 bar. (11) Hydriding by H_2 at 1.01 bar and temperatures below 885°C. (12) PuH_x-catalyzed oxidation by O_2 at 1.01 bar.

Hydride-catalyzed corrosion of Pu initiates spontaneously if metal coated with PuH_x, PuOH, or a Pu_2O_3–PuH_x double layer is rapidly exposed to air at room temperature. Curve 10 defines the rate in air at 0.6 bar because data for 1.0 bar coincides with curve 11 for hydriding. As described by curve 12, hydride-catalyzed oxidation of Pu by O_2 also initiates spontaneously upon rapidly exposure to 1.0 bar O_2.

Thermal ignition of Pu results if metal is heated to 500°C by an external heat source or a chemical reaction. Sufficient heat for ignition may be generated by oxidation of reactive compounds coexisting with the metal [3]. The thermal contribution of chemical reactions in promoting ignition is demonstrated by the behavior of chips and fines. Thermal modeling shows that rapid reoxidation of the Pu_2O_3-rich layer formed on the metal surface by autoreduction of adherent PuO_2 at 150–200°C provides sufficient heat to raise the adiabatic temperature to the 500°C ignition point of Pu if the minimum thickness of the metal is less than 0.1 mm [7]. Measurements at constant ambient temperatures [35] and calculation of the temperature (300°C) at which the rate of heat loss from a Pu surface equals the rate of heat generation by air oxidation [36] show that accumulation of heat from autothermic oxidation of the metal offers a slower alternative ignition path that initiates at ambient temperatures as low as 375°C [35]. Heat apparently accumulates at temperatures in the 300–375°C range, but metal with minimum dimensions of several millimeters oxidizes fully before the 500°C ignition point is reached.

Massive metal coated with PuH_x or PuOH spontaneously ignites upon exposure to air at temperatures as low as 25°C. Self-sustained reaction occurs if the heat generated by initial reaction of O_2 is sufficient to form a catalytic Pu_2O_3 layer at the gas–solid interface. Catalyzed reaction continues until all metal is consumed. PuOH reactivity is markedly altered by the presence of Pu because product hydrogen is accommodated by the metal and does not restrict reaction of O_2.

Enhanced autoreduction of PuO_2 at elevated temperatures, as well as catalytic and transport properties of Pu_2O_3, suggests that thermal ignition in air is triggered by formation of a sesquioxide layer on the metal near 500°C. Self-sustained thermal oxidation (curve 8) is slower than hydride-catalyzed corrosion (curve 10) because the $Pu + N_2$ reaction is prevented by absence of PuH_x catalyst. Burning metal glows like charcoal because the N_2 diffusion barrier at the gas–solid interface maintains a constant oxidation rate.

5. Applications

5.1. Chemistry of stored plutonium

A widely accepted conclusion reached during early studies of moisture-enhanced plutonium corrosion in air is that hydride formed by reaction of water participates in acceleration of the rate [37]. Production of PuH_x by the reaction of H_2O at elevated temperatures is documented [29,38], but its formation in moist air below 200°C is only implied by a 10^2–10^4 fold enhancement of the corrosion rate and the absence of H_2 as a detectable reaction product. O_2 is consumed at the rapid rate of the metal–water reaction, but neither PuH_x nor H_2 is formed. Recent results indicate that reaction of Pu with O_2 in moist air below 200°C is catalyzed via a cycle in which surface PuO_2 reacts with chemisorbed H_2O to form a high-composition oxide (PuO_{2+x}) and hydrogen [24,39,40]. The H atoms produced at the gas–oxide interface combine with dissociatively adsorbed oxygen to reform the water catalyst. Enhanced oxidation is caused by the increase in oxygen concentration associated with PuO_{2+x} formation at the gas–solid interface, not by formation of catalytic hydride at the oxide–metal interface. Corrosion rates in moist and dry air are equal above 200°C where chemisorbed water is unstable.

A more comprehensive view of hydride formation during Pu corrosion in moist air is gained by considering the $Pu + H_2O$ reaction and the effects of temperature on the surface oxide. The protective PuO_2 layer formed by reaction of H_2O vapor at low temperatures prevents product hydrogen from reaching the oxide–metal interface and forming hydride [16,40]. In the absence of O_2, hydrogen appears as H_2 instead of thermodynamically favored PuH_x. The shift in kinetics of the competing redox reactions toward Pu_2O_3 at high temperatures increases the thickness of the sesquioxide layer at the oxide–metal interface and the likelihood of exposing that layer during oxide spallation. An increase in the probability of transporting hydrogen to the oxide–metal interface at elevated temperatures is suggested by the presence of about 15% PuH_x in the $Pu + H_2O$ product at 250°C [29]. Appearance of an accelerating third stage during reaction of Pu with H_2O vapor at 20 mbar and 305°C [41] suggests that formation of Pu_2O_3 is progressively driven by an autothermic process. ‘Slate-like’ mixtures of oxide and hydride are obtained by reacting massive Pu with mixtures of 25% steam and 75% argon at temperatures above 400°C [38]. Although reaction is initiated by external heating, self-sustained reaction and temperatures in the 400–800°C range are maintained by adjusting the H_2O partial pressure in the Ar carrier. PuH_x formation via the $Pu + H_2O$ reaction is apparently promoted by progressive formation of catalytic Pu_2O_3 at elevated temperatures.

Kinetic control of plutonium corrosion in air at normal storage temperatures (<100°C) inherently results in formation of products containing no detectable hydride, but behavior differs in open and closed chemical systems. In an open system, the O_2 source is unlimited, the water-catalyzed $Pu + O_2$ reaction continues as long as O_2 is present, and concurrent formation of PuH_x is unlikely. If a small amount of hydride forms, it resides at the product–metal interface beneath a protective PuO_2 layer [29]. In a closed system, O_2 is first depleted by water-catalyzed oxidation of Pu. The $Pu+H_2O$ reaction then proceeds with formation of additional oxide and H_2. Hydride forms after the reaction of H_2O is complete and autoreduction transforms the PuO_2 layer onto catalytic Pu_2O_3. The time required for PuH_x formation depends on temperature, amounts of available O_2 and H_2O, metal area, and thickness of the PuO_2 layer. The final product is the Pu_2O_3–PuH_x double layer that catalyzes rapid corrosion of Pu by O_2 and N_2 upon exposure to air and accounts for spontaneous ignition of both finely divided and massive plutonium [2,5].

Additional complexity arises if a radiolytic hydrogen source such as plastic or oil is present. If the system is open, H_2 formed by alpha-particle radiolysis of the organic material escapes without altering behavior. If the system is closed, H_2O is formed by combination of H_2 and O_2 on the oxide surface [24,39] and consumed via the $Pu+H_2O$ reaction [39]. The PuO_2 product is transformed into Pu_2O_3 over time and all hydrogen is ultimately transformed to hydride if sufficient Pu is available.

5.3. Control of ignition

Ignition of plutonium via the thermal route is possible if reaction of coexisting compounds upon exposure to air heats the metal to 500°C. The hypothetical corrosion product (94.5% $PuO_{1.98}$, 5% PuH_2, 0.5% Pu grains) proposed in an earlier evaluation [3] is suitable for examining this possibility, even though the likelihood of forming such hydride-rich mixtures appears remote. Relevant reactions and data in Table 3 show that thermal output is dominated by the presence of hydride and that the heat product of the mixture, $\Delta H^\circ_{\mathrm{mix}}$, is 296 J g^{-1} of mixture.

The maximum effect of the reactive mixture on metal temperature is calculated assuming that the reactions in Table 3 are instantaneously complete and that all heat is retained by the PuO_2 product and coexisting massive Pu. The change in temperature (ΔT) is determined by the heat product of the reactive mixture, the heat capacities of dioxide ($Cp_{\mathrm{PuO_2}}$) and metal (Cp_{Pu}), and the mass fraction (f) of reactive mixture:

$$\Delta T = (f\,\Delta H^\circ_{\mathrm{mix}})/[(fCp_{\mathrm{PuO_2}}) + (1-f)(Cp_{\mathrm{Pu}})] \qquad (18)$$

Median values of Cp for PuO_2 (0.293 J $K^{-1}g^{-1}$) and Pu (0.159 J $K^{-1}g^{-1}$) for the 300–1000 K range [42] and the derived heat product show that the maximum temperature increase is 1010 K for oxidation of the mixture ($f=1$). Maximum temperature changes for $f=0.50$, 0.30, 0.25, 0.10 and 0.05 are 656, 447, 385, 173, and 90°, respectively. These conservative results show that more than 30% of the plutonium must exist as this corrosion product in order to raise the temperature from 50 to 500°C and ignite metal with a thickness greater than 0.2 mm. However, only 5–6% of the product is necessary to heat chips and fines from 50 to 150°C.

Ignition is marked by onset of self-sustained reaction and is apparently the temperature at which formation of Pu_2O_3 becomes kinetically favored. The ignition point is also defined by the corrosion rate required to maintain that temperature and is bracketed by the maximum oxidation rate ($\ln R=-4.6$) of curve 4 and self-sustained rate ($\ln R=-2.0$) of curve 8 in Fig. 5. The median value (0.07 g Pu cm^{-2} min^{-1}) is adopted as the best indicator of ignition rate. Curve 7 in Fig. 5 shows that the corresponding temperature is 490°C. In a similar way, rate equations derived in this study define the O_2 pressures required for formation of Pu_2O_3.

Estimation of the ignition pressure for thermal oxidation of Pu in air is based on the general rate equation for the hydride-catalyzed $Pu+O_2$ reaction (Eq. (15)). Effects of a slightly negative activation energy for the process are ignored. Net heat generation is independent of the PuH_x layer at the product–metal interface and the same oxidation rate is required to form Pu_2O_3 during thermal and catalytic ignition. Use of Eq. (15) to calculate the PO_2 corresponding to R of 0.07 g Pu cm^{-2} min^{-1} gives an ignition pressure of 97 mbar or 9.6% O_2 in air. This value is in precise agreement with results of ‘glow time’ tests that measured the length of time a massive Pu sample glowed (reacted rapidly) after it was preheated to 500°C and exposed to a known O_2–N_2 mixture [33]. Exposure to atmospheres with 7 and 9% O_2 resulted in termination of reaction after glow periods of 4 and 6 s, respectively. In contrast, exposure to mixtures containing 10% or greater O_2 concentrations resulted in glow periods of 1–3 min and complete oxidation of the metal. These results support our conclusion that high O_2 pressures produce sufficient heat to form Pu_2O_3 and low O_2 pressures yield protective PuO_2 layers.

Table 3
Reactions and thermodynamic data for oxidizing a mixture of reactive plutonium compounds

Reaction	ΔH° of reaction per[a] unit of solid reactant (kJ mol^{-1})	(kJ g^{-1})	Percentage in mixture	Heat product (J g^{-1} mix)
$Pu+O_2\rightarrow PuO_2$	1056	4.42	0.5	22.1
$PuH_2+3/2O_2\rightarrow PuO_2+H_2O$	891	4.74	5.0	237.0
$PuO_{1.98}+0.01O_2\rightarrow PuO_2$	10.5	0.039	94.5	36.8

[a] Enthalpy of formation data used for calculating ΔH° are from Ref. [26].

In a parallel way, the O_2 pressure required for self-sustained corrosion of Pu by the hydride-catalyzed reaction with air is derived using Eq. (12). The air pressure corresponding to the corrosion rate of 0.07 g Pu cm^{-2} min^{-1} is 0.20 bar or to a PO_2 of 42 mbar. The O_2 pressure is lower than that for thermal oxidation by O_2 because heat is also generated by the accompanying reaction of N_2. Ignition tests show that reactions of Pu filings in nitrogen-rich atmospheres containing 3–5% O_2 initiated near 170°C, but were incomplete [33]. Experience at Rocky Flats shows that pyrophoric behavior is sharply reduced or eliminated in reduced-oxygen (3–5%) glovebox atmospheres. At the nominal atmospheric pressure of 0.81 bar at the site, 3–5% O_2 corresponds to partial pressures of 24–41 mbar. The upper limit of this range agrees with the O_2 pressure above which hydride-catalyzed corrosion apparently produces Pu_2O_3. The lower limit is consistent with data showing that exposure of PuH_x to O_2 at 13.3 mbar results in facile formation of PuO_2 and termination of rapid oxidation [16].

6. Conclusions

In a synergistic way, pyrophoric reaction of plutonium hydride is entwined with chemistry of the surface oxide formed during reaction. Hydride is reactive and oxidizes rapidly upon exposure to oxygen at room temperature. The reaction has zero activation energy, and contrary to expectation, is not autothermic. However, self-sustained pyrophoric reaction with indiscriminate oxidation and nitriding occurs if the O_2 pressure is adequate for initial and continuing formation of catalytic Pu_2O_3. If the O_2 pressure and reaction temperature are too low, rapid reaction terminates as protective PuO_2 forms on the hydride surface.

In addition to commonly cited properties such as specific surface area and heat of reaction, pyrophoricity is determined by other fundamental material properties. Important properties of PuH_x include: a hydrogen transport rate characteristic of superionic conduction, a capacity for accommodating product hydrogen in the solid, and catalysis of nitride formation. Hydride pyrophoricity also depends on equally unusual properties of Pu_2O_3: catalysis of O_2 an N_2 dissociative adsorption, transport of oxygen and nitrogen at rates characteristic of superionic conduction, and a squared dependence of the oxidation rate on oxygen pressure. The pressure exponent is extremely important and apparently results from the interaction of O_2 with Pu_2O_3, but efforts to identify reasonable mechanistic steps consistent with a squared dependence have been unsuccessful.

Hydride-catalyzed reaction of Pu with O_2 and N_2 in air is chemically identical to that of pyrophoric PuH_x. Both processes have zero activation energy and are apparently catalyzed by Pu_2O_3. Rates also vary with the square of O_2 pressure and are independent of N_2 pressure. The only significant difference is the greater capacity for accommodating product hydrogen in metal than in hydride. Kinetic results suggest that Pu_2O_3 promotes dissociative adsorption of H_2, O_2 and N_2 and transports the atomic products at rapid rates. The oxidation rate (78 g Pu cm^{-2} min^{-1}) measured during hydride-catalyzed oxidation of Pu by O_2 [5] corresponds to advancement of the reaction front into delta-phase metal at 3 m h^{-1} and to interfacial hydriding at the rate expected for the $Pu+H_2$ reaction at 1 kbar H_2. These observations imply that, except for the chemical potential driving reaction and failure of Pu to readily react with N_2, chemistry of metal corrosion is determined by properties of the product layer on the surface.

Results of this study and literature data for corrosion of Pu by H_2O suggest that pyrophoric reaction of corrosion products and ignition of metal are strongly dependent on storage conditions. Studies show that PuH_x is not produced by the $Pu+H_2O$ or water-catalyzed $Pu+O_2$ reactions at temperatures below 200°C [24,39,40]. Small amounts of hydride form in the oxide–metal interface at higher temperatures [29], but stoichiometric production of Pu_2O_3 and PuH_2 is expected only as temperatures approach or exceed 500°C. Formation of significant hydride during atmospheric corrosion of metal in open oxygen-rich systems is unlikely and coverage by a protective PuO_2 layer is expected to prevent rapid reaction of PuH_x that might be present at the product–metal interface. Kinetic data suggest that complete oxidation of chips and fines is likely during extended exposure to moist conditions with unlimited oxidant [39]. At 25°C, 0.1-mm thick unalloyed Pu is fully oxidized after 6.5 and 2.6 years in 3 and 30% relative-humidity air, respectively. However, reaction of water in closed or severely oxygen-starved systems ultimately results in formation of the catalytic Pu_2O_3–PuH_x double layer on the metal surface. The likelihood of catalyzed ignition upon exposure to air is high and incidents involving pyrophoric reaction of massive metal and containment failure are documented [2,5].

A fundamental understanding of factors that control the pyrophoricity of plutonium compounds and ignition of the metal is established by this study. The results provide a technical basis for assessing and managing hazards associated with reactivity and ignition during handling and storage of plutonium and plutonium-containing residues.

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