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EFFECT OF WATER VAPOR, REDUCED OXYGEN CONCENTRATIONS,
AND SOLVENT VAPORS ON PLUTONIUM IGNITION

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CONTENTS

Abstract	1
Introduction	1
Experimental	2
Results and Discussion	3
Storage in Humid Atmospheres	3
Reduced Oxygen Concentration	4
Solvent Vapors	5
Conclusions	6
References	7

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EFFECT OF WATER VAPOR, REDUCED OXYGEN CONCENTRATIONS, AND SOLVENT VAPORS ON PLUTONIUM IGNITION

Larry E. Musgrave

Abstract. The effects of water vapor, reduced oxygen concentration, and chlorinated solvent vapor on the ignition of various sizes of samples of unalloyed and alloyed plutonium have been studied. Storing unalloyed plutonium lathe turnings in moist atmospheres reduces the ignition temperature, but storing plutonium 1- wt % gallium alloy lathe turnings in moist atmospheres raises the ignition temperature regardless of the moisture level. Adding nitrogen to reduce the oxygen concentration does not, generally, change the ignition temperature. However, the intensity of the reaction is reduced, and at low concentrations ignition is prevented. The presence of carbon tetrachloride vapor lowers the ignition temperature of plutonium, but the presence of perchloroethylene vapor has no affect.

INTRODUCTION

Experience with plutonium in the nuclear industry shows that, because it has an unpredictable pyrophoricity, plutonium is a severe safety and economic hazard. The violence of some plutonium fires is in contrast to controlled experiments with massive plutonium. Felt¹ found that massive plutonium was extremely difficult to ignite and burns slowly without flame or volatilization. However, other factors must be considered. First, plutonium is difficult to extinguish, requiring argon flooding (which is difficult to accomplish in normal gloveboxes) or heat removal.¹ Second, when combustibles are near plutonium they can easily be ignited by the burning plutonium and cause the fire to spread rapidly. Hence, to control plutonium fires, combustible materials should be removed from plutonium areas. In addition, factors which influence plutonium ignition should be well understood so that conditions which can cause ignition are minimized. This report attempts to extend the understanding of some of these factors.

Plutonium ignition occurs when the heat generated by oxidation (or some other chemical reaction) is greater than the heat which is lost by the metal. Chatfield²

measured the net increase in heat of plutonium during oxidation and developed a semi-empirical theory of plutonium ignition. He predicted that oxidation will not be self-sustaining when the oxygen pressure is reduced below a critical limit. With a delta-stabilized alloy the limit is 0.04 atmospheres, but with unalloyed plutonium the results were dependent on history of the sample.

Others have also studied the ignition of plutonium. Schnizlein and Fischer³ studied the effects of alloying and thickness on ignition behavior of plutonium foils. They found that nominal 2 at. % additives of various elements can raise, lower, or leave the ignition temperature unchanged. The ignition temperature was found to be in two distinct temperature regions — about 300°C and 500°C — depending on the sample thickness, alloy, and oxidizing gas.

Pitts⁴ found that the ignition temperature of screened filings was dependent on the relative surface area and the sample mass. The ignition temperature decreased as the relative surface area increased or as the sample mass increased. He also found that lowered ignition temperatures of plutonium could be induced by stressing, preheating in argon, or lowering the heating rate.

Pitts^{5,6} investigated the reaction of hot plutonium dropped into various chlorinated solvents. He measured light intensity of the reaction and also determined the critical temperature at which a self-sustaining reaction with plutonium can occur.

However, not all factors which can influence plutonium ignition have been studied. In this study the effects of the following atmospheres on plutonium ignition are reported:

- The presence of water vapor in the air for extended periods of time,
- the oxygen concentration in nitrogen, and
- the presence of solvent vapor in air and in air-nitrogen mixtures.

EXPERIMENTAL

The ignition temperatures of the samples were determined by the burning curve method.⁷ Figure 1 shows a schematic of the apparatus. The sample was placed on a spoon inside a Vycor tube. It was heated at a 30°C temperature rise per minute with a tube furnace. The sample temperature was monitored with a platinum/platinum-13% rhodium thermocouple placed inside the spoon. At ignition, the sample temperature rose rapidly. The heating rate curve, and the temperature curve following ignition, were graphically extrapolated as shown in Figure 2. The intersection of these curves is the ignition temperature. Gases or vapors surrounding the sample were controlled by continuous flow of the proper mixture through the Vycor tube.

Figure 1. Apparatus for determining the ignition temperature.

An additional device used to measure the effect of oxygen concentrations on plutonium ignition is shown in Figure 3. Plutonium coupons were ignited by placing them on a heater maintained at 500°C. A Vycor bottle through which a gas mixture flowed was placed over the sample until glowing ceased. The time between placing the bottle over the sample and the cessation of glowing is the "glow" time.

Plutonium used in these studies was either unalloyed or delta-stabilized (Pu 1-wt% Ga). All samples weighed about 0.5 grams. Coupons were wire brushed and cut to size (about 1.0 by 0.5 by 0.1 cm³). Those used to study oxygen concentration effects had been stored for about 2 weeks in a moist atmosphere and appeared dark. Those used in the other studies had

Figure 2. Ignition temperature curve of a 0.50 gram coupon of plutonium 1-wt% gallium alloy.

Figure 3. Apparatus for determining the glow time of burning plutonium in oxygen deficient atmospheres.

been stored in dry air (200-700 ppm H₂O) and appeared shiny. The delta-stabilized lathe turnings were about 2.0 by 0.1 by 0.02 cm³. The unalloyed lathe turnings were about 0.2 by 0.2 by 0.02 cm³. Oil was removed from the lathe turnings by washing them in carbon tetrachloride. The filings were obtained from a clean, delta-stabilized coupon. The filing was done in a dry air glovebox (200-700 ppm moisture). They were collected between 300 and 140 mesh screens. All filings were tested within 24 hours to reduce surface oxidation.

Gases used were compressed air and bottled nitrogen. Flow was regulated and measured with a flowmeter. Mass spectrometry was used to analyze the oxygen concentration. Solvent vapors were obtained by bubbling the gas mixtures through reagent grade carbon tetrachloride or perchloroethylene. Mass spectrometer analysis showed the solvent vapor concentration to be near saturation at room temperature.

RESULTS AND DISCUSSION

Storage in Humid Atmospheres

The effect of storage time, humidity level, alloying agent, and relative surface area upon the ignition temperature of plutonium was studied. Samples, of unalloyed plutonium and plutonium 1-wt%gallium alloy coupons and lathe turnings, were stored in desiccators. Relative humidity of about 1 percent was maintained by using CaCl_2 pellets, about 33 percent using saturated solutions of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, or about 60 percent using NH_4NO_3 . Coupons were removed from desiccators after 2-, 5-, and 7- weeks and ignited. Lathe turnings were removed from the desiccators after 2-, 4-, and 6- weeks and ignited.

The ignition temperatures of the coupons, shown in Figure 4, were virtually unchanged regardless of humidity. However, the lathe turnings show significant changes in ignition temperature with humidity level. The unalloyed plutonium lathe turnings ignited at lower temperatures after storage in moist atmospheres, as shown in Figure 5. The ignition temperatures of the plutonium 1-wt% gallium alloy lathe turnings are shown in Figure 6. The ignition temperature of the alloy gradually increased regardless of the humidity level in the storage atmosphere. Figure 6 shows that the ignition temperature increased from 270°C to over 310°C in the 6-week period. Later experiments with the same material (alloy lathe turnings) showed that the ignition temperature had increased to nearly 350°C after storage for 4 months in dry air (300-700 ppm moisture).

The variations in the ignition temperature of the lathe turnings after exposure to moist atmospheres is due largely to variations in oxidation rates in such atmospheres. Unalloyed plutonium is known to oxidize much more rapidly in moist atmospheres than in dry air. In addition, fragmentation may occur.⁵ Small additions of gallium to plutonium, however, tend to slow corrosion in moist atmospheres to a rate only slightly greater than that in dry air. The oxide established is protective.⁹

Figure 4. Ignition temperatures of plutonium coupons stored in different humid atmospheres.

Figure 5. Ignition temperatures of unalloyed plutonium lathe turnings stored in different humid atmospheres.

The unalloyed lathe turnings showed the effect of severe oxidation and fragmentation. Toward the end of the experiment the samples which had been stored in humid atmospheres appeared powdery. In fact, the sharp declines in ignition temperature occurred when the samples were mostly powder (very few intact chips). These powders would have a higher relative

Figure 6. Ignition temperatures of plutonium 1-wt% gallium alloy lathe turnings stored in different humid atmospheres.

surface area, and therefore, as shown by Pitts⁴, have a lower ignition temperature. In addition, extensive moisture corrosion leaves reactive PuH_2 on a plutonium surface.^{10, 11} Plutonium hydride (PuH_2) is pyrophoric and may also lower the ignition temperature.

The plutonium 1-wt% gallium alloy lathe turnings demonstrated a lesser rate of corrosion, only being darkened by 6- weeks storage in humid atmospheres. The ignition temperature gradually increased, probably as a result of the build-up of a protective oxide.

The constant ignition temperature of the plutonium coupons appears in contrast to the previously mentioned corrosion effects. The coupons, however, have a lower relative surface area for corrosion, and the protective oxide on the gallium alloyed plutonium is less effective at higher temperatures. Hence, the observations were not unexpected.

The unalloyed plutonium coupons which were stored in moist atmospheres failed to show evidence of fragmentation for as long as 7 weeks. However, they did appear severely oxidized and an increase in storage interval would probably result in fragmentation. Fragmentation would radically lower the ignition temperature. In addition, the low relative surface area decreases the influence that PuH_2 has on the ignition temperature. Therefore, extended storage in moist atmospheres is not desirable.

Reduced Oxygen Concentration

Samples of plutonium 1-wt% gallium alloy coupons, lathe turnings and filings were heated in flowing air-nitrogen mixtures. The temperature rise following ignition gradually decreased as the oxygen concentration was decreased. This made it difficult to determine when ignition occurred for samples in atmospheres containing less than about 5-percent oxygen. (The concentrations depended on the relative surface area of the samples.) Hence, a temperature rise of 50°C or more is necessary for a reaction to be termed ignition. Reactions in which the temperature rise was less do not appear to be self-sustaining as shown by the glow-time measurements with coupons.

The ignition temperatures of the different samples in various oxygen concentrations are given in Tables I to III. For oxygen concentrations below 7-, 5-, and 3- percent no ignition is observed for coupons, lathe turnings, and filings, respectively. The glow-time measurements, for coupons in various oxygen concentrations, are given in Table IV which shows that the reaction is rapidly extinguished with oxygen concentrations up to 9 percent.

Table I. Ignition temperature of 140 mesh plutonium 1-wt% gallium fillings in various concentrations of oxygen.

Ignition Temperature ($\pm 10^\circ\text{C}$)	Oxygen Concentration (vol%)
175	20 $\pm$ 1
183	12 $\pm$ 1
165	8 $\pm$ 1
170*	5 $\pm$ 1
160*	3 $\pm$ 1
No reaction	<1

*Samples were not completely burned and could be re-ignited in air after cooling.

Table II. Ignition temperature of plutonium 1-wt% gallium lathe turnings in various concentrations of oxygen.

Ignition Temperature ($\pm 10^\circ\text{C}$)	Oxygen Concentration (vol%)
265	20 $\pm$ 1
270	12 $\pm$ 1
400	8 $\pm$ 1
Slight reaction at 270°C	5 $\pm$ 1
No reaction	3 $\pm$ 1
No reaction	<1

Table III. Ignition temperature of plutonium 1-wt% gallium coupons in various concentrations of oxygen.

Ignition Temperature ($\pm 10^\circ\text{C}$)	Oxygen Concentration (vol%)
505	20 $\pm$ 1
510	10 $\pm$ 1
No ignition (slight reaction)	6 $\pm$ 1
No ignition (very slight reaction)	5 $\pm$ 1
No ignition	< 1

Table IV. Glow time of plutonium 1-wt% gallium coupons in various concentrations of oxygen.

Glow Time (± 0.1 min)	Oxygen Concentration (vol%)
0.03	< 1
0.03	4 $\pm$ 1
0.04	6 $\pm$ 1
0.06	7 $\pm$ 1
0.10	9 $\pm$ 1
1.0	10 $\pm$ 1
1.5	20 $\pm$ 1

The ignition temperature of coupons and filings showed no significant change when the oxygen concentration was lowered to where ignition did not occur. However, the ignition temperature of the lathe turnings changed from 270°C to 400°C when the oxygen concentration was changed from 12- to 8-percent. The thickness of the turnings is about the same as that found by Schnizlein and Fischer to be the dividing point between ignition in the low and high temperature regions in air.³ Evidently, the lower oxygen concentration changes the ignition temperature from the lower to the higher region.

For filings, the temperature rise after ignition decreased as the oxygen concentration was lowered. (See Figure 7.) This is due to one of the following reasons: (1) decrease in the reaction rate with complete reaction, (2) a change in the oxide formed, or (3) incomplete reaction of the plutonium.

The reaction was shown to be incomplete by performing the following experiment. Alloyed plutonium filings were heated in 3- and 5-percent oxygen atmospheres to about 600°C , with ignition occurring at 170°C . However, after cooling, the samples were reheated in air and ignited at about 200°C .

The incomplete reaction may be caused by the formation of PuO . Pitts⁴ observed PuO to form when plutonium coupons were heated in argon containing about 1% oxygen at 500°C . Some badly deteriorated samples demonstrated ignition temperatures in air of about 200°C . The deteriorated coupons probably

offer about the same surface area as the filings, and the similar ignition temperature indicates similar surface conditions. It is possible that the PuO retards reaction in low oxygen atmospheres (below about 5-percent oxygen) but not in air.

Figure 7. The effect of reduced oxygen concentrations on the ignition temperatures and maximum temperatures of 140 mesh plutonium 1-wt% gallium alloy filings.

The lathe turnings and coupons appeared nearly intact following ignition in low oxygen concentrations. It is likely that they also were incompletely reacted. However, the maximum temperature was not reproducible because of the placement of the thermocouple, and there was no attempt to re-ignite samples.

Solvent Vapors

The effect of solvent vapor on the ignition of plutonium 1-wt% gallium alloy lathe turnings was studied in air-nitrogen mixtures. The gas mixture was bubbled through carbon tetrachloride achieving a volume concentration of about 10%, or through perchloroethylene achieving a volume concentration of about 1.5%. The ignition temperatures and maximum temperatures in various oxygen concentrations were measured for each of the solvents. The results are listed in Table V along with the results with no solvent vapor present. Figure 8 shows the gradual change in ignition temperature and maximum temperature as oxygen concentration is varied in atmospheres containing carbon tetrachloride vapor.

Table V. Ignition of plutonium 1-wt% gallium in solvent vapor atmospheres.

Oxygen Concentration (vol%)	Solvent (vol%)	Ignition Temperature ($\pm 10^\circ\text{C}$)	Maximum Temperature ($\pm 20^\circ\text{C}$)	Time of Reaction (min)
20 $\pm$ 1	none	270	550	0.1
20 $\pm$ 1	10% CCl_4	200	440	3.0
20 $\pm$ 1	1.5% C_2Cl_4	270	570	0.1
5 $\pm$ 1	none	slight reaction		
5 $\pm$ 1	10% CCl_4	255	400	1.5
5 $\pm$ 1	1.5% C_2Cl_4	slight reaction		
3 $\pm$ 1	none	no reaction		
3 $\pm$ 1	10% CCl_4	280	330	0.5
<1	10% CCl_4	slight heating above 400° *		
<1	1.5% C_2Cl_4	no reaction		

*An additional exotherm was observed when the samples were heated to 650°C . The exotherm is probably caused by a reaction with CCl_4 vapors.

Figure 8. The effect of reduced oxygen concentration and carbon tetrachloride vapors on the ignition and maximum temperatures of plutonium 1-wt% gallium alloy lathe turnings.

These results show that the presence of carbon tetrachloride vapor significantly affects the ignition of plutonium in air-nitrogen mixtures. The ignition temperature is lowered 70°C in air. Ignition occurs in a 3-percent oxygen concentration when carbon tetrachloride vapors are present, but it does not occur when carbon tetrachloride vapors are absent. Furthermore, the time of reaction is lengthened when carbon tetrachloride vapors are present.

The increased likelihood of ignition is in contrast to the lower maximum temperature recorded when carbon tetrachloride vapors are present. The 100°C temperature decrease in maximum temperature was accomplished by a longer time of reaction in air;

that is, from 0.1 minute to 3.0 minutes. It appears that the burning is slowed, but not stopped.

Leibowitz, Schnizlein, and Mishler¹² have observed a similar effect when uranium is ignited with halogenated hydrocarbons in the air. They advanced several possible causes which should be applicable to plutonium. The organic vapors or their breakdown products were: (1) poisoning the reaction surface, (2) rendering the surface oxide more protective, or (3) competing for the limited supply of oxygen. The ignition and burning observed in 3-percent oxygen, only when carbon tetrachloride vapors are present, rules out the competition hypothesis. If the burning was slowed by simple dilution or by reaction of the organic with oxygen, then it would be expected that burning would cease in higher oxygen concentrations when carbon tetrachloride vapors are present. This was not observed.

Evidence of a plutonium-carbon tetrachloride reaction was given by an exotherm at about 650°C when bottle nitrogen and carbon tetrachloride were flowed through the ignition apparatus.

The failure of perchloroethylene vapor to affect the ignition characteristics of the plutonium is not surprising. There is nearly an order-of-magnitude less vapor present (1.5 vol% to 10 vol%). In addition, Pitts^{5,6} found that perchloroethylene is less reactive with plutonium than carbon tetrachloride. There is nearly a 200°C temperature difference in the critical temperature of reaction with coarse 1-wt% gallium alloy filings.

CONCLUSIONS

This study has shown that plutonium ignition and burning is affected by: (1) exposure to water vapor over a period of time, (2) the oxygen concentration in the surrounding atmosphere, and (3) carbon tetrachloride vapor. The ignition temperature, the maximum temperature during burning, and the time the reaction is sustained are all dependent on the atmosphere.

Storage in water vapor decreases the ignition temperature of unalloyed plutonium lathe turnings. This is due to fragmentation of the sample and formation of reactive corrosion products. However, plutonium 1-wt% gallium alloy shows a slight increase in ignition temperature when stored, regardless of the presence of water vapor. This is probably caused by the formation of a protective oxide.

Coupons showed no change in ignition temperature when stored in moist air atmospheres. However, unalloyed coupons could show a significant decrease if they were stored long enough for fragmentation to occur.

Reducing the oxygen concentration by adding nitrogen to air gradually lowers the intensity of the oxidation reaction. Oxygen concentrations below 7-, 5-, and 3-percent prevent the ignition of plutonium 1-wt% gallium alloy coupons, lathe turnings, and filings, respectively.

The presence of carbon tetrachloride vapors, even in low oxygen concentration atmospheres, causes a decrease in the ignition temperature of plutonium 1-wt% gallium alloy lathe turnings and also causes ignition in oxygen concentrations as low as 3%. The presence of perchloroethylene in various atmospheres has no effect on the ignition of plutonium 1-wt% gallium alloy lathe turnings.

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