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OBSERVATIONS ON THE ATMOSPHERIC OXIDATION
OF PLUTONIUM METAL

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The effects of temperature, pressure, and moisture on the atmospheric oxidation of plutonium metal have been investigated. Changes in the slope and a discontinuity have been confirmed in the oxidation rate curve at temperatures of the plutonium phase transformations. The minimum in the rate curve near 400°C was reconfirmed. Properties of the oxide and metal possibly contributing to the anomalous oxidation behavior have been considered.

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OBSERVATIONS ON THE ATMOSPHERIC OXIDATION OF PLUTONIUM METAL

1. Introduction

1.1. The oxidation rates of unalloyed plutonium metal have been measured at temperatures up to 450°C in air and oxygen under varying conditions of pressure and moisture. Several apparent anomalies in the rate curves have previously been observed. These include a discontinuity at the beta to gamma phase change with a significantly lower rate at the higher temperature¹ and a decrease in the rate above 325°C with a minimum at 400°C^{1,2,3,4,5}.

1.2. Previous studies have shown no correlation between the corrosion rate decrease and the oxide lattice parameter, oxygen to plutonium ratio, density, crystalite size or particle size¹. This study was conducted to examine more critically the effect of temperature, pressure and moisture on the oxidation rates of plutonium. In addition, oxide properties were investigated by differential thermal analysis in an attempt to relate oxide properties to the oxidation rates.

2. Experimental

2.1. Plutonium oxidation measurements were carried out on a Cahn-vacuum-recording microbalance with an associated vacuum system to control the atmosphere to which the sample was exposed. The gas pressure was controlled to ± 0.5 Torr

by evacuating the balance and vacuum system and backfilling to the required pressure. The high moisture content gases were normal laboratory air and tank oxygen. The moisture content of the dry air and oxygen were controlled with the aid of a drying tube on the gas filling system. Low moisture concentrations were measured with a model W Meeco moisture analyzer. The gas was static during a single measurement. The volume of the balance was large compared to the gas consumed so that the pressure remained essentially constant throughout the run.

2.2. Heating of the gas and the sample was accomplished by a resistance tube furnace on the outside of the balance hangdown tube. Temperature calibration showed the measured sample temperature to be in error by less than $\pm 5^{\circ}\text{C}$ over the range 25° to 600°C . The sample was heated in the controlled atmosphere in order to prevent the formation of a protective layer (possibly PuO) which has been shown to form when plutonium is heated in a low partial pressure of oxygen¹.

2.3. Metal used in the corrosion studies was from a rolled sheet. Samples were cut and filed to the desired size. Total surface area of each sample was approximately one cm^2 . All samples were taken from the same original sheet having an average total spectrographic impurity content of 870 ppm and a density of 19.414 g/cc. Gas analysis by vacuum fusion showed 4.1 ppm hydrogen and 23.9 ppm oxygen.

2.4. Differential thermal analysis studies of plutonium oxide were made on a Harrop DTA instrument with the furnace enclosed in a drybox to prevent contamination spread. The oxide used in the investigation was prepared by air oxidation at 25°C of the previously described metal.

3. Results and Discussion

3.1. Effect of Temperature

3.1.1. In general, plutonium corrodes by two or more linear rates (reaction controlled) below 220°C, and an initial parabolic rate (diffusion controlled), followed by a linear rate, above 220°C^{1,5,6}. A linear rate generally continues until breakaway occurs.

3.1.2. Figure 1 shows the linear corrosion rates of plutonium in 620 Torr of air and of pure oxygen. Time to establish this rate varied from a few minutes at high temperatures to 17 or more hours at low temperatures. The maximum time of corrosion measurement was 100 hours. The moisture content of the air was approximately 10^4 ppm (8.4°C dew point) and of the oxygen was between 40 and 1000 ppm. Figure 1 represents the range and estimated best curve for 63 separate measurements. The maximum variation in corrosion rate is about a factor of ten which is in the range reported by other investigators.

3.1.3. Changes in the slope at the alpha to beta and gamma to delta phase transformations and the discontinuity at the

FIGURE 1 - The Linear Oxidation Rates of Unalloyed Plutonium Metal in Air and Oxygen
(Moisture content of air, 10^4 ppm, and of O_2 , 40-1000 ppm)

beta to gamma transformation are apparent. Since these changes coincide with the metal phase changes, it is thought that changes in properties of the metal or changes in the metal properties in relation to the oxide formation are responsible. The particular property of the metal or oxide responsible for these changes has not been established. It has been suggested that changes in the phase or thermal expansion of the oxide are responsible for the rate decrease above 350°C with a minimum at 400°C⁵. Other studies¹ showed no relation between the rate decrease and the oxide lattice parameter, oxygen to plutonium ratio, crystalite size, particle size, or density. Differential thermal analysis of the oxide formed at 25°C, as discussed in section 3.4., failed to suggest any oxide property that is related to this anomalous rate decrease.

3.1.4. At 220°C, where the discontinuity is observed, the oxidation mechanism changes from two linear rates to a parabolic-linear rate. The parabolic-linear reaction suggests an initial formation of a lower oxide which, after reaching a limiting thickness, oxidizes to a higher oxide at a linear rate. A similar mechanism has been observed for the oxidation of zirconium carbide⁷ and for tungsten⁸. Close examination has revealed the presence of a lower oxide (Pu_2O_3) at the

plutonium surface when oxidation occurs at high temperatures⁹. The calculated thickness of a lower oxide in the 220° to 450°C range, based on the weight change at the time the linear rate is established and a penetration of 3.77 u per 1 mg/cm² of corrosion¹⁰, is 1 to 10 microns. This is less than the thickness of 50 microns estimated by Schnizlein and Fischer in the 220° to 320°C range⁵.

3.1.5. The points near the upper limit of the curve in Figure 1 are generally for oxygen. The higher rates in oxygen possibly reflect the oxygen pressure dependence of the reaction; however, experimental variation was sufficiently great that this could not be positively established from this data. Average activation energies based on the extremes of these rates are as follows:

<u>Phase</u>	<u>Temperature Range</u>	<u>Activation Energy</u>
alpha	25 - 120°C	23 kcal/mole
beta	120 - 209°C	12 kcal/mole
gamma	209 - 320°C	14 kcal/mole

Schnizlein and Fischer reported an activation energy of 16 kcal/mole for a single process from 140° through 300°C⁵.

Sackman has attributed the large variation in oxidation rates, and hence activation energies, to such factors as texture and the distribution of impurities¹¹.

3.2. Effect of Moisture

3.2.1. Figure 2 shows the linear oxidation rates of plutonium in very dry air and in pure oxygen as compared to the rates in moist air. The generally observed large effect of moisture is not as apparent at high temperatures, as at room temperatures (25°C). The times to establish the linear rates, however, were significantly longer in the dry atmosphere. The decrease in the rates at about 120°C was observed in both dry air and dry oxygen. This phenomenon was not observed in an atmosphere containing 50 ppm H₂O. If the oxidation rates are radically changed by changes in oxide properties, it might be expected that the rates would be parabolic (diffusion controlled) rather than linear. This is possibly the case as a long, relatively flat parabolic curve over a long period of time is difficult to distinguish from a linear curve. Waber reported a parabolic curve over 1000 hours in very dry air changing to a linear rate with increasing moisture¹⁰.

3.2.2. It is well known that metal stored in a moist atmosphere will corrode considerably faster than that stored in a dry atmosphere. Two mechanisms have been proposed to explain this effect. The hydride mechanism¹² postulates that metal hydride formed by the reaction of moisture with the metal will react with additional moisture to form the oxide. Part of the released hydrogen will then react with the metal to replace the hydride according to the following reactions:

FIGURE 2 - The Effect of Moisture on the Linear Oxidation Rates of Unalloyed Metal.

Waber has proposed an anodic control mechanism involving diffusion by hydroxyl ions and the formation of an intermediate Pu(III) hydroxide species which oxidizes to the tetravalent oxide¹⁰.

3.2.3. Reaction studies of plutonium metal and water vapor at 100° and 200°C have shown that 80 to 85% of the available hydrogen is consumed, and that the corrosion product contains an appreciable amount of hydride as well as the oxide¹. This supports the "hydride" mechanism, which does not explain the relatively large effect of small amounts of moisture. A possible explanation of this is that hydride which is formed by a reaction of metal and moisture (Eqs. 4 and 5) reacts with oxygen to give oxide and additional water (Eqs. 6 or 7) rather than reacting with moisture (Eq. 3).

3.2.4. The oxidation of the hydride was studied by thermogravimetric analysis in very dry air and in moist air between 120° and 240°C. A moisture increase was observed in the gaseous products. A slightly greater weight gain than would be expected from total conversion to the dioxide was also observed suggesting adsorbed moisture. An activation energy of about 18 kcal/mole was calculated for the reaction in dry air.

3.2.5. In moist air the activation energy for the oxidation of the hydride was found to be only 9 kcal/mole, slightly less than that found for the linear oxidation of the metal in moist air in the same temperature range. At 240°C the rate of hydride oxidation was shown to be less than at 200°C, similar to the measured metal oxidation rates (Figure 1). Since the activation energy of the reaction between the hydride and very dry air (Eq. 6 or 7) is relatively high, a second intermediate is suggested involving a reaction between the hydride and the moisture. The following mechanism could explain the presence of the hydride in the corrosion product, the effects of small amounts of moisture and the measured activation energies.

The rate controlling step for the process would be the hydride-moisture reaction (Eq. 10).

3.2.6. Acceleration of the oxidation by moisture in the parabolic or diffusion controlled region can be explained in terms of the less dense hydride intermediate producing a more porous oxide layer or diffusion path.

3.3. Effect of Air Pressure

3.3.1. Figure 3 shows the differences in the oxidation rates of plutonium in moist air (104 ppm H₂O) at 50, 150, and 620 Torr. It can be seen that the effect is not consistent over the entire temperature range. At lower pressures the rate decrease at 320°C appears to be minimized or eliminated.

3.3.2. The pressure dependence of the reaction at 230°C is approximately given by:

$$R = 4.01 \times 10^{-2}P - 4.31 \times 10^{-4}P^2$$

This relation holds, however, only at this temperature. At 400°C an inverse pressure effect is observed. A more detailed investigation of the reaction and reaction products is required to understand the effect.

FIGURE 3 - Effect of Pressure on the Linear Oxidation Rates of Unalloyed Metal.

3.4. Oxide Properties

3.4.1. Plutonium oxide formed from the oxidation of unalloyed metal in air at 25°C was compared to aluminum oxide by differential thermal analysis as described in section 2.4. At least three exotherms, as seen in Figure 4, were observed at approximately 120, 160, and 220°C. The origin of these peaks has not been positively established, but several possibilities are suggested from the following observations:

- (1) The exotherms are not repeated after the oxide has been heated to 900°C indicating an irreversible process.
- (2) The exotherms are again observed if oxide heated to 900°C is mixed with plutonium metal filings and reheated in air.
- (3) An impure argon atmosphere will eliminate the 160°C peak and decrease the size of the 220°C peak.
- (4) Plutonium filings alone heated in air will show an exotherm at 220°C.
- (5) Heated oxide mixed with plutonium metal and reheated in an argon atmosphere will show only the phase changes of the metal (endotherms).

FIGURE 4 - Differential Thermal Analysis of Plutonium
Oxide Formed at 25°C.

3.4.2. Based on these observations and previous studies showing the formation of lower oxides during corrosion³, the following is suggested:

- (1) The exotherm at 120°C appears to be unaffected by heating the original oxide in an argon atmosphere. It is eliminated when the heated oxide is remeasured with plutonium filings, in an argon atmosphere. It is suggested that a transformation of alpha-Pu₂O₃ to beta-Pu₂O₃ or some other undefined transformation of a lower oxide is occurring at this temperature. Chikalla, et al.¹², have concluded that the oxygen deficient solid solutions, PuO_{2-x}, undergo eutectoid decomposition at approximately 300°C to form the alpha-Pu₂O₃, demonstrating the possibility of a low temperature transformation.

- (2) The exotherm at 160°C is completely eliminated in an argon atmosphere suggesting a reaction such as

An impure Pu_2O_3 formed by the carbon reduction of PuO_2 at 1700°C was heated in air at $5^\circ\text{C}/\text{min.}$ on a recording microbalance. Oxidation was observed to start at 170°C . A total weight gain of 3.31% was measured. Pure Pu_2O_3 would be expected to gain 3.04%, if totally converted to PuO_2 . It is thought, therefore, that some PuO , stabilized by the carbon, may have also been present and been converted to PuO_2 .

- (3) The 220°C exotherm is suggested as an accelerated oxidation of unreacted metal within the oxide. This has previously been observed in ignition studies¹. Unreacted metal is observed by x-ray diffraction of the oxide formed at 25°C and is suggested by the endotherm at the melting point (640°C) of the metal (Figure 4). Metal could be contained within a coating of oxide if the oxidation attack is intergranular and if the oxide is protective, or if the reaction is extremely

slow after the oxide attains a critical thickness. This accelerated oxidation could be associated with the discontinuity in the corrosion rate curve. Sackman⁶ and Waber¹⁴ found a weight increase after complete oxidation greater than would be expected from the formation of stoichiometric PuO_2 . They attributed this to adsorbed moisture.

3.4.3. The exotherms at 120° and 220°C correspond to the temperatures of the rate changes in the oxidation curve (Figure 1). Further study will be required to more definitely establish the oxide properties causing the exotherms and to relate them to the metal oxidation.

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