Oxidation of Delta-Phase Plutonium Alloy:

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Humid Air at 35°C

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ABSTRACT

Kinetic data for oxidation of delta-phase plutonium alloy are evaluated to provide a technical basis for assessing the merit of an existing time limitation on air exposure of components during process operations. Data describing the effects of humidity and oxygen pressure on the oxidation rate of the Pu-1.0 wt % Ga alloy at elevated temperatures are obtained from literature sources and used to predict the oxidation behavior of the alloy in air at 35°C and 0 to 100% relative humidity. A mandated six-hour limit on air exposure is inconsistent with a predicted thirty-day period required for formation of a 1-μm-thick oxide layer in moisture-saturated air at 35°C. Relationships are defined for predicting kinetic behavior of the alloy at other conditions, and recommendations for addressing oxidation-related concerns in production are presented.

INTRODUCTION

Various questions and issues have arisen during efforts to establish pit fabrication capabilities at Los Alamos. In the absence of nuclear testing for verifying pit function, precise duplication of production procedures employed at Rocky Flats is desirable and justified. In some instances, processes cannot be reproduced because of changes in regulations or the unavailability of essential materials. In other cases, duplication of processes appears feasible. However, in all cases, evaluation of the rationale for existing procedures is prudent and necessary for establishing the relevance and value of specific procedural requirements imposed during production at Rocky Flats.

An effort is made in this report to determine if a technical basis exists for placing a six-hour limit on the time period that a clean (oxide-free) plutonium component may be exposed to air between process operations. The procedure also requires that the oxide formed on the surface of the delta-phase plutonium component during production not exceed a thickness of 1 μm. A limitation on maximum oxide thickness is reasonable for the operation involved and is accepted as a valid requirement. However, technical evaluation is needed to determine if the time and thickness constraints are consistent and

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to assess the need for retaining a six-hour exposure limit, a requirement that apparently has existed for approximately thirty years.

A technical assessment is possible using data from recently published reports by Stakebake and coworkers on the corrosion kinetics of the Pu-1 wt % Ga alloy in air [1], oxygen [2], and water vapor [3] at elevated temperatures. In this evaluation, the thickness of the oxide formed on the surface of clean alloy at 35°C is calculated as a function of time during exposure to dry and humid air. A predictive method is necessary because air oxidation rates for the alloy are slow and have been measured only at elevated temperatures. The results are compared with other observations and their relevance to production conditions are discussed.

REVIEW AND ANALYSIS OF LITERATURE DATA
The Oxidation Process

Oxidation of clean plutonium in air is a two-step process described as "paralinear." Whereas the extent of reaction follows a parabolic time dependence during the initial stage of oxidation, the behavior is linear with time during the second stage [2,4]. If a clean plutonium surface is exposed to oxygen, the extent of the initial reaction follows a time dependence characteristic of a diffusion-controlled process. The rate of oxidation is determined by the rate at which oxygen diffuses through the layer of product oxide formed on the metal and progressively decreases as the thickness of that layer increases over time. During the parabolic step, the extent of reaction (E_t) is proportional to the square root of time (t) as described by Equation 1:

$$E_t = E_0 + k_p t^{1/2}. \tag{1}$$

E_0 is a constant that defines the extent of oxidation for the parabolic process in units of mg oxygen /cm^2 and is zero for clean plutonium. Throughout this report, k_p defines the parabolic rate constant in units of mg oxygen /cm^2 min$^{1/2}$.

The second step of plutonium oxidation is entered when the adherent oxide layer begins to crack. At the onset of this step, stresses generated between the low-density oxide layer and high-density metal are sufficient to fracture the oxide and cause the spallation of oxide particles. Localized enhancement of the oxidation rate occurs at these cracks and spallation sites. As the oxide thickness increases at these locations, the resulting decrease in rate is offset by cracking and spallation at other locations. The net process establishes a constant average layer thickness and a constant bulk reaction rate defined by the linear E_t–t relationship in Equation 2:

$$E_t = E_0 + k_l t. \tag{2}$$

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In this case, E_0 defines the apparent extent of oxidation for the linear process at zero time. The linear rate constant k_l defines the rate of oxidation for the linear step in units of mg oxygen /cm^2 min.

Correlation of reaction temperature with the steady-state oxide thickness present during the linear step [5] suggests that only the parabolic step of oxidation is pertinent to issues addressed in this report. The thickness, x, of the adherent oxide layer on plutonium varies with T as defined by the Arrhenius-like relationship in Equation 3:

$$\ln x = 6.95 - (1{,}673/T). \tag{3}$$

At the steady-state temperature of 35°C (308 K) estimated for a typical plutonium component in a glovebox environment, x has a value of 4.6 μm. This thickness includes the dimensions of a coherent (uncracked) layer near the oxide-metal interface and of a cracked layer at the air-oxide interface. Because a large fraction of the oxide particles formed by air oxidation of plutonium at room temperature has maximum dimensions less than 3 μm [6], the minimum thickness of the coherent layer probably equals or exceeds 2 μm. Therefore, the 1-μm thickness of concern for production processing is apparently reached during the parabolic stage of oxidation and kinetic behavior during the linear process is not pertinent.

As shown by variations in the rate constant, the oxidation rate of plutonium in air is a function of temperature, oxygen pressure, and water pressure[7]. The general kinetic relationship for a parabolic process is given by Equation 4:

$$k_p = k\text{'}\exp(-E_a/2R^*T)\,(PO_2)^m(PH_2O)^n. \tag{4}$$

The experimentally-determined proportionality constant is given by k'. The exponential Arrhenius term includes the activation energy (E_a) and describes the temperature dependence of the rate; m and n define the dependence on pressures of oxygen (PO_2) and water (PH_2O), respectively. Values of k_p may be calculated for a given PO_2 and PH_2O at other temperatures if the Arrhenius relationship is known for those pressures.

The dependences of k_p on PO_2 or PH_2O are defined by isothermal measurements in which the second pressure is fixed. At constant T and PO_2, the parabolic rate constant is related to the water pressure by the proportionality constant k' as shown in Equation 5:

$$k_p = k_p\,(PH_2O)^n. \tag{5}$$

A similar equation relates k_p to PO_2 and m. Values of m and n are defined by experimental results and are applied in adjusting k_p values for differences in oxygen or water pressure. Observations for unalloyed Pu show that the oxidation rate at room temperature is independent of PO_2 if PH_2O is greater than 0.5 ppm (3.8×10^{-4} torr) [7]. A similar independence of k_p on PO_2 is assumed for the 1.0 wt % Ga alloy.

Parabolic kinetics are observed for the reaction of delta-phase plutonium alloy with both oxygen [1, 2] and water vapor [3]. Oxidation rates in humid air or water vapor are inherently faster than in dry air or dry oxygen [7]. Experimental rates for the alloy-O_2 reaction are available only for temperatures in excess of 150°C and measurements for alloy and H_2O extend to 100°C. Therefore, extrapolation of results obtained at high temperatures is necessary in order to define kinetic behavior at 35°C. Adjustments for effects of water pressure on the rate are also necessary. The assumption is made that the kinetics of both reactions remain parabolic at temperatures below the experimental ranges.

Temperature Dependence of the Parabolic Rate Constant

The dependence of k_p for oxidation of the 1.0 wt % Ga alloy by dry oxygen at 500 torr pressure is described for the 150 to 500°C range by Stakebake [1]. The Arrhenius relationship derived from graphical data and the reported E_a value of 21 ±1 kcal/mol is given by Equation 6:

$$2\ln k_p = 14.0 - (10{,}500/T). \tag{6}$$

At 35°C and $PO_2 = 500$ torr, k_p is 4.3×10^{-5} mg/cm^2 min$^{1/2}$. Estimation of the uncertainty suggests that this extrapolated value may be high or low by a factor of two.

Arrhenius results for reaction of the alloy with water vapor at 15 torr pressure at 100 to 540°C are reported in a parallel publication [3]. The activation energy is 15.1 ± 0.6 kcal/mol. The temperature dependence of k_p is described by Equation 7:

$$2\ln k_p = 9.1 - (7550/T). \tag{7}$$

At 35°C and $PH_2O = 15$ torr, k_p is 4.5×10^{-4} mg/cm^2 min$^{1/2}$, an order of magnitude greater than in dry oxygen.

Pressure Dependence of the Parabolic Rate Constant

The dependence of the parabolic constant on oxygen pressure is described by Stakebake and Lewis [2]. Values of m are reported for several temperatures and for O_2 pressures in the 0.01 to 500 torr range. For PO_2 less than 10 torr, m is zero and k_p is independent of oxygen pressure. Non-zero values of m appear at pressures above 10 torr, but the dependence is weak and decreases as the temperature is lowered. The values of m at 400, 300, and 200°C are 0.25, 0.20, and 0.14, respectively. The magnitude and trend established by these data suggest that m is small at room temperature and that changing PO_2 from the 500 torr to the 160 torr partial pressure of an air atmosphere does not significantly alter the parabolic rate constant. This assessment is verified by calculations which show that this pressure reduction lowers k_p by about 15% if m equals 0.14 at 35 °C. In light of a possible two-fold error from temperature extrapolation, the pressure effect is

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extremely small and the k_p value of 4.3×10^{-5} mg/cm^2 min$^{1/2}$ accurately defines the parabolic oxidation of delta-phase alloy in dry air at 35°C.

Effects of water pressure on k_p are reported by Stakebake and Saba [3]. The behavior is similar that for oxygen. Results for 300°C and PH_2O in the 0.1 to 15 torr range indicate that k_p is independent of water pressure below 1.5 torr. At higher pressures, $n = 0.15$. If this value of n is applicable at lower temperatures, increasing the PH_2O from 15 torr to the equilibrium (saturation) pressure of 42 torr at 35°C increases k_p by approximately 17%. The adjusted k_p value for oxidation of delta-phase alloy in 100% relative humidity (RH) air at 35°C is 5.2×10^{-4} mg/cm^2 min$^{1/2}$.

Parabolic rate constants for humidity levels between extremely dry and saturated conditions are necessary for assessing the validity of the time constraint. The dependence of k_p on PH_2O is derived by assuming that the parabolic rate constant is independent of PO_2 under humid conditions and follows the logarithmic form of Equation 5. Values of k_p for O_2 and H_2O at 35°C are obtained by extrapolation Equations 6 and 7. At 35°C, the k_p values for dry oxygen and for 15 torr water pressure are 4.3×10^{-5} and 4.5×10^{-4}, respectively. A value of 7.6×10^{-3} torr (10 ppm) is adopted for the water pressure in dry oxygen because that concentration was determined for similar kinetic data measured with the same microbalance equipment and procedures [7]. The resulting relationship for oxidation of delta-phase alloy in air at 35°C is given by Equation 8:

$$\ln k_p = -8.54 + 0.31 \ln PH_2O. \tag{8}$$

This equation incorporates the water-pressure dependence of the parabolic rate constant, but gives a somewhat larger n than reported by Stakebake [3]. According to Equation 8, k_p for water-saturated air at 35°C is 6.2×10^{-4} mg/cm^2 min$^{1/2}$.

RESULTS

The time-dependent oxidation of 1 wt % Ga alloy in air at 35°C is bounded by the oxidation rates for dry and water-saturated conditions. Values of k_p defined for the entire humidity range by Equation 8 were used with Equation 1 to calculate extents of reaction. Results for selected humidities and periods of exposure to air are presented in Table 1 as units of oxide thickness. For these calculations, the metal surface was assumed to be clean ($E_0 = 0$) at zero time and the product layer was assumed to be plutonium dioxide (PuO_2) with a density of 11.45 g/cm^3.

Table 1. Predicted Time and Temperature Dependence of Oxide Thickness on the Pu-1 Wt % Ga Alloy in Air at 35°C

| Time | | Oxide Thickness (μm) | | | |
min	days	0% RH[a]	1% RH	10% RH	100 % RH
0	0	0	0	0	0
6	0.004	0.0008	0.003	0.005	0.011
60	0.041	0.0025	0.008	0.017	0.036
180	0.12	0.0043	0.014	0.029	0.061
360	0.25	0.0060	0.020	0.041	0.087
600	0.41	0.0078	0.025	0.053	0.11
6000	4.1	0.025	0.081	0.17	0.36
60000	41	0.078	0.14	0.53	1.12

a. The estimated water concentration at 0% RH is 10 ppm.

CONCLUSIONS

Results in Table 1 indicate that the six-hour limit on air exposure of a clean delta-phase plutonium component is inconsistent with the constraint on oxide thickness. An exposure period of approximately thirty days is required to form a 1-μm-thick oxide layer on the alloy at 35°C and 100% RH. Humidity levels in the facility are well below saturation and vary from about 1% RH in winter to 10% RH in summer [8]. Because of the factor-of-two uncertain in k_p, the period required to reach a given thickness may be half or twice the indicated time, but the inconsistency in the requirement remains unresolved.

As shown by ellipsometric results reported by Larson and Cash [9], formation of the oxide layer is accompanied by distinct color changes associated with optical interference. The oxide thicknesses and the corresponding first-order interference colors observed with an incandescent light source are listed in Table 2. Correlation of the thickness data in Tables 1 and 2 shows that the characteristic gold color of a 0.04-μm-thick oxide is expected to appear after 6 hours in air at 10% RH and after 24 hours in air at 1% RH.

The observed oxidation behavior of delta-phase alloy in a production facility may differ substantially from the predictions in Table 1. The calculated values are based on experimental data obtained with high-purity reactants under carefully controlled conditions. Factors that might alter the corrosion rate of the alloy include gas-phase

contamination and alloy composition. Indeed, corrosion rates encountered in the production lines at Rocky Flats probably differ from the predicted values in Table 1. Gaseous hydrochloric acid (HCl) formed by reaction of water with chlorocarbon cleaning solvents was present because all galvanized surfaces in the glovebox lines were transformed into zinc dichloride ($ZnCl_2$) over time. The effects of HCl and other species that may have enhanced or suppressed corrosion in the production environment are unknown.

Table 2. Correlation of Plutonium Oxide Thickness in Delta-Phase Pu with Color[a]

Color	Oxide Thickness (μm)
neutral silver	0.0100
gold	0.0400
red-violet	0.0525
violet	0.0575
purple	0.0600
blue	0.0800
silver-blue	0.1000

a. Data are the first-order interference colors reported in Reference 9.

RECOMMENDATIONS

Assessment of corrosion kinetics in this report leads to the following recommendations:

1. The justification for a six-hour limitation on exposure of a component to air, which appears inconsistent with kinetic data for oxidation of the alloy, should be reviewed.

2. In all likelihood, the corrosion rates of the alloy in the glovebox environment of PF-4 differs from the predicted oxidation rates presented in this report. Therefore, implementation of experiments to measure the time-dependent color changes of alloy samples at several locations in the glovebox line is recommended. This exercise would help in determining the need for exposure limitations in production. A photographic record of the tests would provide a semiquantitative measure of corrosion rates, help identify glovebox locations with corrosion-enhancing

atmospheres, and provide a baseline reference for assessing changes in corrosion behavior over time.

3. Rather than implementing corrective action to remove excess oxide from components, an alternative approach based on avoidance of the problem is recommended. The need for an oxide removal process and for a limitation on air exposure is a consequence of the procedures used at Rocky Flats. A cleaning process was needed to remove excess oxide because machined and inspected components with clean surfaces were stored in air for extended periods before subsequent operations. Use of a sealable, controlled-atmosphere container for storing components between process operations would prevent formation of a thick oxide layer, eliminate the need for oxide removal, and reduce the risk of mechanical damage during handling.

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