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Review of Plutonium Oxidation Literature

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Summary

A brief review of plutonium oxidation literature was conducted. The purpose of the review was to ascertain the effect of oxidation conditions on oxide morphology to support the design and operation of the PDCF direct metal oxidation (DMO) furnace. The interest in the review was due to a new furnace design that resulted in oxide characteristics that are different than those of the original furnace. Very little of the published literature is directly relevant to the DMO furnace operation, which makes assimilation of the literature data with operating conditions and data a convoluted task. The oxidation behavior can be distilled into three regimes, a low temperature regime (RT to 350°C) with a relatively slow oxidation rate that is influenced by moisture, a moderate temperature regime (350 – 450°C) that is temperature dependent and relies on more or less conventional oxidation growth of a partially protective oxide scale, and high temperature oxidation (> 500°C) where the metal autocatalytically combusts and oxidizes. The particle sizes obtained from these three regimes vary with the finest being from the lowest temperature. It is surmised that the slow growth rate permits significant stress levels to be achieved that help break up the oxides. The intermediate temperatures result in a fairly compact scale that is partially protective and that grows to critical thickness prior to fracturing. The growth rate in this regime may be parabolic or paralinear, depending on the oxidation time and consequently the oxide thickness. The high temperature oxidation is invariant in quiescent or nearly quiescent conditions due to gas blanketing while it accelerates with temperature under flowing conditions. The oxide morphology will generally consist of fine particles (<15 µm), moderately sized particles (15 < x < 250 µm) and large particles (> 250 µm). The particle size ratio is expected to be < 5%, 25%, and 70% for fine, medium and large particles, respectively, for metal temperatures in the 500-600°C range.

Overview of select articles

Numerous articles and reports indicate that room temperature oxidation in air and moisture will result in a fine oxide film that appears as interference bands initially then forms a powdery surface that ultimately culminates in olive green PuO_2, The explanation for this oxide growth mode is that the surface may form hydrides as well as oxides and there is sufficient strain development that the oxides are mostly smaller than 30µm (1). There are additional articles which indicate the powdery form does not occur and the oxide grows thick enough (5-15µm) to being spalling due to the high residual stress (2, 3, & 4).

In addition, moisture has a significant impact on the oxidation rate and particle size distribution at low temperatures (<350°C).

Evaluation of the oxidation characteristics at elevated temperature provides less concise results. There are situations reported that show particulate sizes are in excess of 3 mm for oxidation at temperatures of 500°C (5). Within this report, the particle size is reported as a bimodal particle size distribution due to the strain related fracture of the oxide resulting in spallation of large (>150 µm) of oxide and associated fines from fracture (<10 µm). In fact, this report indicates 87% of the particles are greater than 150µm and 27% could be greater than 1 mm. The proposed oxidation rate at temperatures in excess of 500°C in static air is predicted to be $0.16\underline{+}0.08$ g PuO_2 / cm^2*min (approximately 0.07 mm/min). In ref. 6 the particle size distributions for unalloyed Pu oxidized at 25°C and 500°C were 0.6 and $5x10^{-4}$, respectively, for the mass fractions of particles with a diameter of less than 10µm. Unfortunately, this result is attributed to an unpublished account / personal communication with T.E. Ricketts, 1996 (Ref 22 of Ref. 6).

The oxidation behavior is also dependent on the Pu component size. Small pieces may ignite at lower temperatures (5, 6, 7, 8, & 9) due to higher surface area and the need for less sensible heat input. In addition the presence of deformation may reduce the ignition temperature. This reduction can be attributed to the cracking of oxide films and presenting fresh metal surfaces to the oxygen environment. Consistent with oxide effects, the presence of a bulk Pu_2O_3 layer can reduce ignition temperatures since the oxidation of this oxide is also exothermic. However, this reaction is not likely to cause autothermic oxidation since the energy released is not typically sufficient to raise the bulk metal temperature to the temperature required (greater than 500°C $\underline{+}$ 25°C) to promote self sustained oxidation. In addition, the ignition temperature is influenced by the gas composition. It has been shown (10 & 11) that at Pu chips will not ignite in 5% O_2 but will ignite in 8% O_2 at 400°C.

Much of the available literature is based on reviews of other documents rather than experimental results so definitive answers are not always apparent, as indicated previously. Wick (12) and Stewart (13) report that moisture plays an important role at low temperatures. The moisture effect is largely non-existent above 350°C. The Wick (12) compilation correlates oxidation temperature with oxide color such that at 470°C the oxide is brown, 487°C no color was provided, but oxidation rate increased and “was catastrophic” after five hours, 500°C oxide was black and granular, while at 520°C it was black and granular with powder. The comparison of oxide product color may be of interest to see if there is any agreement and to see if the furnace temperature or more critically, the metal temperature, can be inferred.

Mahoney and Mishima (14) reviewed much of the literature to develop a basis for modeling the releases for plutonium oxidation with the express purpose of looking for particles that are finer than 10 µm. The primary goal of this effort was to determine the state of information to model aerosol releases. There is a fairly comprehensive review of the literature especially as it pertains to Pu release, i.e., oxidation and generation of particles less than 10µm in diameter. Within this review, there is recognition that pure Pu oxidizes more rapidly than delta Pu and forms a more friable oxide than the more adherent oxide on the delta Pu. A smaller oxide particle is expected for material that is “jostled” during oxidation that for one that is quiescent. Another consideration that is acknowledged to produce different effects is the metal temperature with at least one report indicating larger particles with higher oxidation temperatures and others reporting the converse. A final consideration is the effect of temperature measurement location

on oxidation product, since measurements can be made by the furnace controller, at the metal surface or internal to the metal. These data all provide different values and this can impact the ability to cross correlate.
As has been suggested, much of the data really are not directly relevant to the purpose of producing plutonium oxide in a controlled burning manner with the express goal of ensuring 99+% oxide formation in a relatively short period of time and with a size distribution after milling of 99% > 5 µm, majority between 50 and 100µm and 100% < 200µm. However, several simple assumptions can be made to estimate the burn rate and the amount of oxygen required to consume nominal Pu-Ga alloy.
The data presented in Table 1 were taken from Figure 2 of ref. 5. The density of PuO_2 was taken as 11.46 g/cc and then the rates for what are termed stage II, linear oxidation behavior and stage III, paralinear oxidation, (see Figure 1) were converted from a mass to thickness basis for both oxide growth and metal recession. This results in thickness based rate constants which can be used to estimate furnace run times provided there is adequate oxygen flow to not starve the process and that the rates do not change significantly with oxide film growth. These rates, based on bulk metal temperatures, not the surface temperature or the furnace temperature, reveal a 16 to 500 times rate increase in going from 450°C to 600°C, depending on whether the material is oxidizing in the stage II or stage III oxidation regime, respectively.

Data from Mishima, Ref. 15, is are presented in Table 2. These data provide size distributions for various oxidation conditions with ignition temperatures ranging from 490 to 500°C. The reaction temperatures varied from nominally 500-660°C, with excursions from 395°C on the low end to 930°C on the high. The data clearly show that the higher temperature oxidation test, data set A Table 2, results in slightly fewer fine oxides being formed, the rationale being that the oxide sinters and becomes more dense and less prone to fracture. The relatively high fraction of small particles shown in data set B Table 2 is attributed to a wider range of temperature swing since the ignited metal extinguished and cooled to 395°C prior to being reheated to ignition. It was suggested that this thermal swing caused increased stress and subsequent particulate cracking.

Laurinet (16 and 17) calculated the oxidation rate and conditions for burning Pu in a confined volume. One outcome of the calculation is that the oxidation rate will be oxygen transport limited, in the cases described in Refs. 10 and 11, it is stack limited, i.e., the Pu is placed in pile and the oxygen has to diffuse through the oxide layer and particles to reach virgin metal, while in the case of DMO it will be oxide scale thickness limited.

Based on this review and my understanding of current operating conditions, it appears that the presence of a consistently finer oxide from DMO-1 compared to DMO-2 may be attributed to 1. more oxidation at lower metal temperature for DMO-2 resulting in thicker oxide surface initially with less opportunity to ignite at the nominal temperature 2 inadequate total oxygen for DMO-2 resulting in incomplete burning. 3. more constant furnace temperature in DMO-2 resulting in less thermal cycling and less strain and consequently less particle generation, and 4. a difference in feed stock -- e.g., hydrided pieces for DMO-1.

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Table 1. Rates estimated from Ref. 5 for a 100 cm^2 surface.

Rate	450	500	550	600
II g PuO2/cm^2/min	6.00E-03	0.01	0.05	0.1
III	0.1	0.5	4	50
	450	500	550	600
	II	II	II	II
Rate g/min (O_2)	6.00E-01	1.00E+00	5.00E+00	1.00E+01
Rate cc/min (oxide)	5.24E-02	8.73E-02	4.36E-01	8.73E-01
Rate cm/min (0xide thickness)	5.24E-04	8.73E-04	4.36E-03	8.73E-03
	III	III	III	III
Rate g/min (O_2)	1.00E+01	5.00E+01	4.00E+02	5.00E+03
Rate cc/min (oxide)	8.73E-01	4.36E+00	3.49E+01	4.36E+02
Rate cm/min (0xide thickness)	8.73E-03	4.36E-02	3.49E-01	4.36E+00
Rate cm/min Pu	3.37E-04	5.61E-04	2.80E-03	5.61E-03
Rate cm/min Pu	5.61E-03	2.80E-02	2.24E-01	2.80E+00

Table 2. PSD and oxidation conditions from Ref. 14—samples were rods

Data Set	**A**	**B**	**C**	**D**	**E**	**F**
Sample mass	9.8944	10.5398	10.9014	11.203	11.2796	11.3423
Length	1.73	1.89	1.85	1.89	1.89	1.89
Diameter	0.602	0.594	0.625	0.625	0.625	0.625
Surface Area	6.00	6.49	6.43	6.55	6.55	6.55
Ignition T	490	490	495	495	500	500
Ox temp Range	480	410	630	630	535	520
Max	560	560	650	650	560	590
Peak	900	560	650	560	560	560
Oxidation time	22	38	30	62	61	64
% oxide recovered	98.8	99.8	97.4	100	99.4	100
% oxide < 250 um	7.72	18.23	8.04	10.25	12.47	12.22
% oxide < 125 um	3.57	7.66	3.05	4.27	5.03	4.95
% oxide < 74 um	2.39	3.75	1.76	2.64	2.96	2.84
% oxide < 44 um	0.99	2.63	1.17	1.76	1.89	1.81
Total < 250 um	14.67	32.27	14.02	18.92	22.35	21.82
15 < ox < 45 um	0.66	0.8	0.68	0.63	0.6	0.76

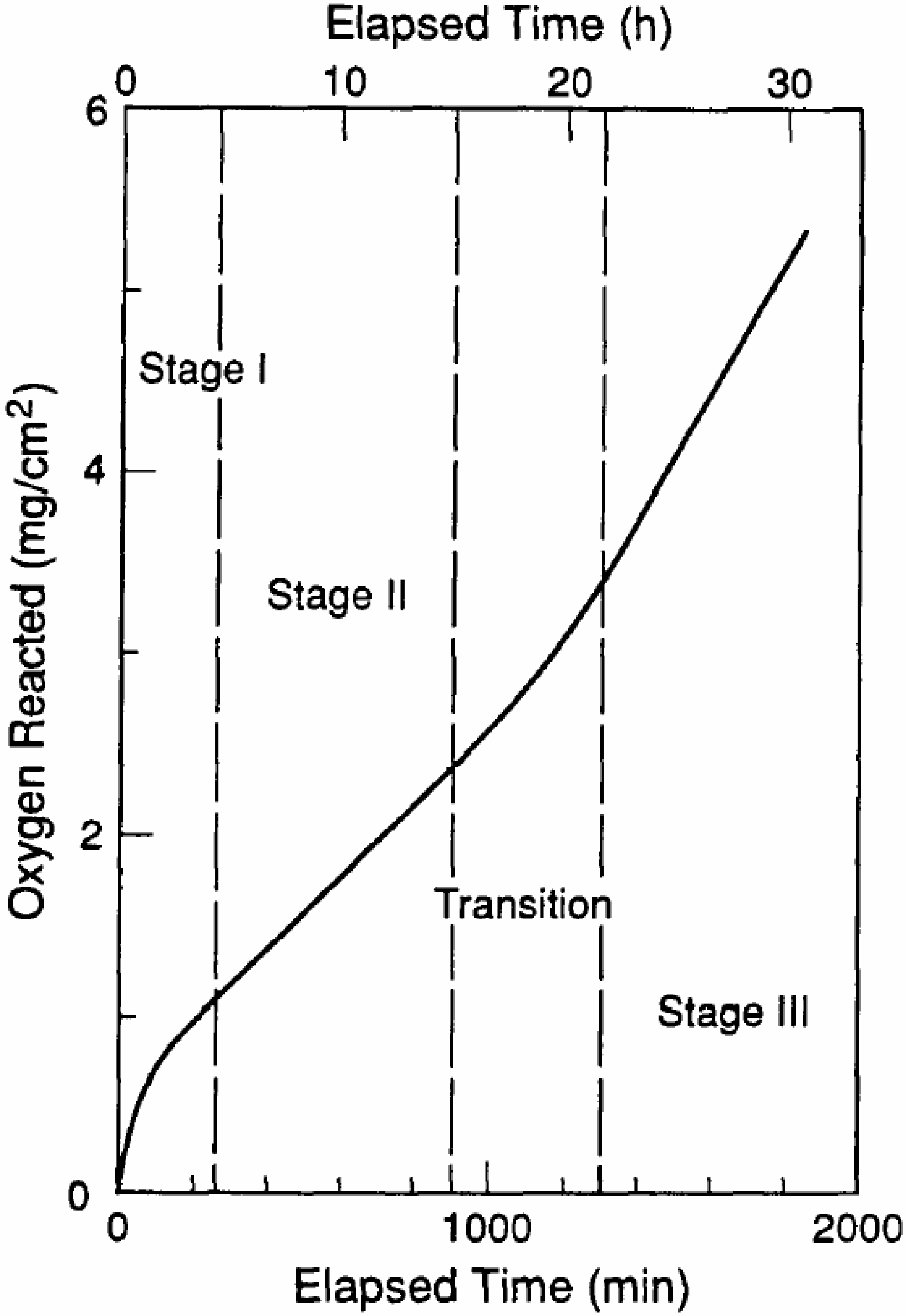

Figure 1. Diagram of oxidation stages for Pu metal at 300°C and 1 Torr Oxygen, Ref 18.