Plutonium Metal: Oxidation Considerations and Approach

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FOREWARD

Plutonium is arguably the most unique of all metals when considered in the combined context of metallurgical, chemical, and nuclear behavior. Much of the research in understanding behavior and characteristics of plutonium materials has its genesis in work associated with nuclear weapons systems. However, with the advent of applications in fuel materials, the focus in plutonium science has been more towards nuclear fuel applications, as well as long term storage and disposition. The focus of discussion included herein is related to preparing plutonium materials to meet goals consistent with non-proliferation. More specifically, the emphasis is on the treatment of legacy plutonium, in primarily metallic form, and safe handling, packaging, and transport to meet non-proliferation goals of safe/secure storage. Elevated temperature oxidation of plutonium metal is the treatment of choice, due to extensive experiential data related to the method, as the oxide form of plutonium is one of only a few compounds that is relatively simple to produce, and stable over a large temperature range. Despite the simplicity of the steps required to oxidize plutonium metal, it is important to understand the behavior of plutonium to ensure that oxidation is conducted in a safe and effective manner. It is important to understand the effect of changes in environmental variables on the oxidation characteristics of plutonium. The primary purpose of this report is to present a brief summary of information related to plutonium metal attributes, behavior, methods for conversion to oxide, and the ancillary considerations related to processing and facility safety. The information provided is based on data available in the public domain and from experience in oxidation of such materials at various facilities in the United States. The report is provided as a general reference for implementation of a simple and safe plutonium metal oxidation technique.

ACRONYMS and NOTATION

The following terms are defined as used in the context of this document:
α-Pu: Unalloyed plutonium metal in the monoclinic crystal structure Alpha-phase,
δ-Pu: Delta-phase plutonium metal, or gallium δ-stabilized plutonium alloy.
alpha-N: Low atomic weight element reaction of emitting a neutron after absorption of an alpha particle
DOE: Department of Energy
Ga: Gallium
LANL: Los Alamos National Laboratory
LME: Liquid Metal Embrittlement
MC&A: Material Control & Accountability
Pu: Plutonium
PVC : Polyvinyl Chloride
SMIE: Solid-Metal Induced Embrittlement
SRNL: Savannah River National Laboratory
SRS: Savannah River Site
TIGR: Thermally Induced Gallium Removal

The following units of measure are used in this report:
°C: Temperature in degrees Celsius
cc: Volume in cubic centimeters
cm: Length in Centimeters
g: Mass in grams
Kg: Mass in kilogram
mm: Length in Millimeters
μm: Length in Micrometers
min: Time in Minutes
hr: Time in Hours

TABLE OF CONTENTS

1.0 METAL FORM METALLURGICAL CHARACTERISTICS

Plutonium metallurgy has only been under development in a few countries since the 1940s. In contrast, the metallurgical science of steel has been developed in many countries for well over a hundred years, and major discoveries continue to be made. While basic plutonium research does continue to occur, the emphasis of this paper is related to the conversion of plutonium metal into a more stable oxide form, and the material characteristics likely to be encountered during conversion, which are well documented. The following subsections provide a basic discussion of the metallurgical characteristics of plutonium metal that are important for consideration when developing an approach for conversion from metal to an oxide.

1.1 Phase structure characteristics and behavior [1,2,3,4]

Plutonium, atomic number 94 in the actinide series of the periodic table, was discovered in 1941 by G.T. Seaborg, who named the element after the 9th planet in our solar system. Early scientific studies, performed using microgram quantities, found that the properties of plutonium are very sensitive to impurities. For example, the earliest studies listed density with a large bimodal spread of either 16 or 20 grams per cubic centimeter. As purity requirements were developed and refined, convergence to the pure Pu material properties was achieved. Pure, or unalloyed, plutonium metal has 6 allotropes, or solid phase forms with different crystal structures, at ambient pressure between room temperature and its' approximate melting point of 640ºC. Table 1 lists the various allotropes, or phases, of Pu metal along with the temperature range of stability, crystal structure (i.e, dictates engineering properties of material), and density.

Table 1: Unalloyed Plutonium Metal Allotropes

Plutonium Allotrope	Ambient Pressure Temperature Range of Stability (ºC)	Crystal Structure	Density (g/cc)
α	<120	Simple Monoclinic	19.86
β	120-210	Body-Centered Monoclinic	17.70
γ	210-315	Face-Centered Orthorhombic	17.14
δ	315-450	Face-Centered Cubic	15.92
δ'	450-480	Body-Centered Tetragonal	16.00
ε	480-637+/-5	Body-Centered Cubic	16.51
L	>637+/-5	Liquid	16.65+

Review of the data in Table 1, along with the linear expansion variation with temperature graph in Figure 1, clearly identify the extremely non-linear behavior of pure Pu as it changes phase structure. Similar variable behavior, such as brittle to malleable crystal structure transition with increasing temperature, density increasing with melting followed by a linear increase of molten liquid density with temperature, and a large range of densities for the various allotropes, are evident upon examination of the figure and table. Figure 1 also includes similar data for iron to compare and emphasize the unique characteristics of Pu. The characteristic of large changes in length, and hence volume, as a function of temperature, makes α-Pu very difficult to fabricate or form into shapes without defects. The large volume change behavior of α-Pu, coupled with the brittle monoclinic crystal structure at ambient temperature, results in cracks, and voids during casting or other heat related fabrication procedures where the temperature is increased above 120°C. In addition to the problems associated with elevated temperature α-Pu processing, liquid plutonium is extremely reactive, corrosive, and has the greatest known surface tension and viscosity among metals due to electron bonding behavior. All of these characteristics present challenges for treatment and containment of plutonium during casting processes. In summary, pure non-alloyed plutonium is very difficult to work with as a material of construction due to extreme changes in characteristics as a function of temperature.

1.2 Plutonium Alloys [1,2,5,17]

The pursuit for stability and formability defined the path for early Pu metallurgical research. The brittle crystal structure and thermal expansion properties of α-Pu cause forming problems. The δ phase allotrope possesses a crystal structure that is malleable, and experiences significantly reduced volume change over

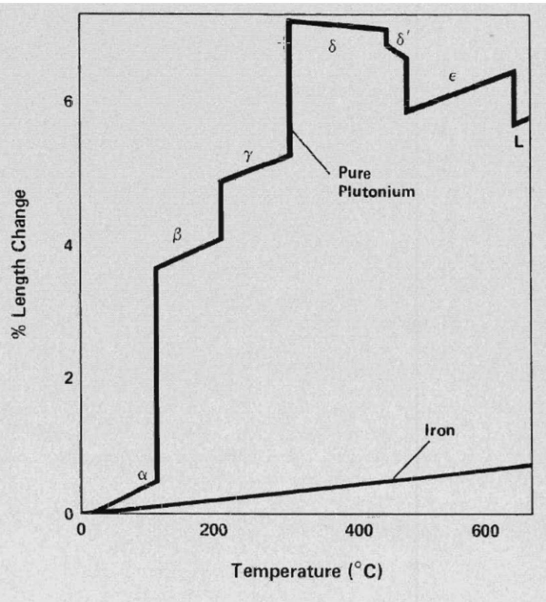


Figure 1: Temperature Distribution of Plutonium Allotropes at Ambient Pressure [1]

the temperature range of stability. Initial studies in alloying Pu recognized that stabilizing to form δ-Pu phase, at room temperature, would alleviate the challenges with shape forming α-Pu. Aluminum was initially found to stabilize δ–Pu at room temperature. However, aluminum is an element that results in the alpha-N reaction where it gives off a neutron upon absorption of an alpha particle from Pu radioactive decay. This neutron emission proved problematic for applications where total control of neutron emission was critical to performance. For this reason, aluminum was essentially abandoned as an alloying element to obtain δ–Pu material. Gallium was found to produce a δ–Pu alloy at room temperature with the malleability and strength of aluminum, but without the alpha-N problem. The gallium stabilized δ–Pu alloy was found to have a density of ~15.7g/cc, and could be hot-pressed into shapes without crack formation during cooling. Gallium alloyed δ–Pu is stable over a temperature range of at least −75 to 475 °C for a moderate ~1-9 atomic % gallium addition.

While other alloying elements were determined to stabilize pure plutonium to δ–Pu (e.g., cerium, americium, indium and scandium), the gallium stabilized alloy was selected for further development, and has the most significant data set available for reference. Figure 2 shows the result of 2 different levels of gallium alloying on the percent length change for the resulting alloy, as compared to unalloyed Pu metal. Basic research of Pu alloys has shown that most alloys are metastable in many environments due to the complex electron bonding behavior of plutonium, but while scientifically significant, were not found to improve the practical use of Pu. Some of the Pu alloy research results are important in regard to impacts on processing or containment. Iron, nickel, or cobalt alloyed with Pu can reduce the melting point of the resulting alloy dramatically, forming a eutectic. Table 2 lists the lowest melting point temperature for eutectics of Pu and various elements commonly used in containment material alloys. Other than carbon, aluminum and gallium, all alloying elements produce eutectics with melting points significantly below that of pure Pu. This result is important when considering a containment device for use while heating Pu metal. For example, plutonium metal heated above 410°C in iron alloys like stainless steel will melt through the steel by forming a eutectic. Even when present in small amounts, the alloying elements can cause local melting or embrittlement at temperatures close to the eutectic temperature due to segregation of the alloy elements in the bulk Pu material.

While not typically used as an alloying element, the open literature indicates that nickel has been used for additional protection against Pu oxidation, and also to provide radioactivity containment. Nickel coating was performed using nickel tetracarbonyl gas. The gas reacts with the plutonium surface and deposits a thin layer of nickel to provide both shielding and oxidation resistance. Processing of nickel coated Pu metal should consider the potential for 465ºC melting point eutectic containment if heating or oxidation of the metal is planned.

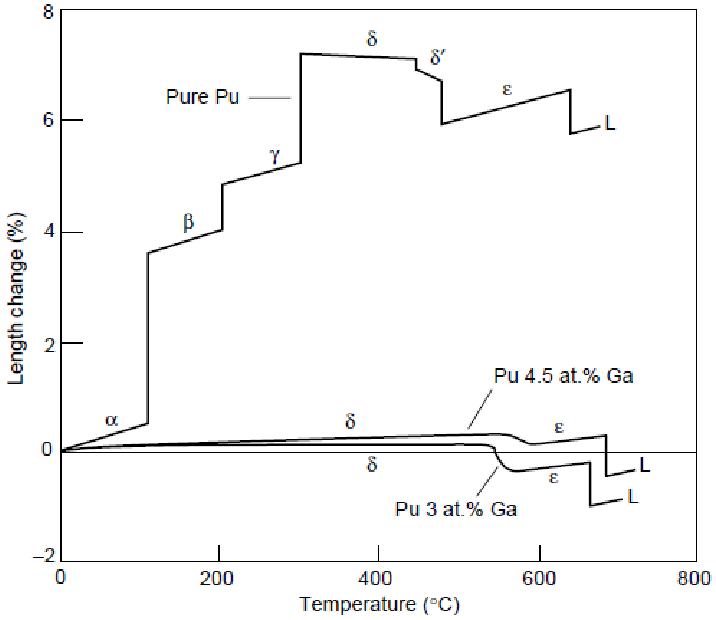


Figure 2. Unalloyed and Gallium Alloyed Plutonium Length Change vs. Temperature [6]

Table 2: Plutonium Binary Alloy Minimum Melting Temperature [17]

Alloy Element	**Pu Alloy Minimum Melt Temperature (°C)**	**wt% Pu**
Aluminum	650	98.4
Carbon	640	100
Chromium	620	99.16
Cobalt	405	97
Copper	625	97
Iron	413	96
Gallium	640	100
Manganese	510	97.7
Nickel	465	96.7
Silicon	590	99.4

1.3 Reactivity, Instability and Storage [3,5,7,8,9,10,13]

The discussion in this section must be prefaced with a suggestion related to safe handling/processing of Pu metal that has been in storage for an extended period of time, and has unknown surface reactivity. Storage conditions will dictate surface reactivity of Pu metal when it is removed from storage for treatment. Exposure to an oxygen limited, nitrogen, or hydrogen atmosphere while in storage, may result in a reactive metal surface condition, and may require special handling considerations. In an oxygen limited environment, oxide on the surface of Pu metal will undergo auto-reduction, or conversion to a different higher oxide (e.g., PuO_2 converts to Pu_2O_3), as the metal mass reaches an equilibrium state. PuO_2 is the stable oxide form in an oxygen rich environment, while higher oxides of Pu tend to be very reactive, and will react quickly if exposed to surplus oxygen. In addition to formation of reactive surface oxides during storage, isotopic composition of the metal, presence or absence of hydrides on the surface, or alloy type may not be thoroughly established. To mitigate potential safety issues associated with reactive surface conditions, it is important that any metal of unknown/uncertain alloy/isotope, or surface condition, be first exposed to a dry argon gas environment when removed from storage, and kept in argon until the reactivity of the metal surface can be determined. Specifically, movement of Pu metal into an oxygen rich, nitrogen, or moist atmosphere should be avoided if surface reactivity is unknown, unless controls, as discussed in section 2.2.4, are in place to deal with ignition of the metal, or gas generating reactions that are discussed in this section.

The nonmetallic elements important when considered for reaction with plutonium are oxygen, carbon, nitrogen, and hydrogen. Oxygen, carbon and nitrogen form high-melting point intermetallic compounds when they react with Pu. Hydrogen reacts readily with Pu, but the compounds readily decompose, resulting in concerns related to long term storage of Pu metal where hydrogen is available for reaction. Formation and reactivity of Pu metal surface hydrides and nitrides, and subsequent reaction with oxygen, are the focus of this section, as oxidation of Pu metal is covered in detail in the next section. Surface carbides are also known to be very reactive as fine powders, but are not discussed here due to the special processing required to make them, as opposed to the formation of hydrides and nitrides than can occur during normal storage conditions. Where polyvinyl chloride (PVC) has been used as containment, degradation has occurred where gaseous HCl or chlorine gas has been evolved. In some cases where PVC was inside of a stainless steel can, corrosion of the can due to the evolved gases occurred. Oxides stored with PVC had to be calcined to remove absorbed chlorine, and repackaged in chloride free systems. In contrast to PVC, polyethylene damage by radiolytic and thermal degradation will occur without the evolution of corrosive gases. Experience and historical storage data gives no indication that decomposition of polyethylene will lead to container pressurization, corrosion of metal containers or degradation of stored material quality [3].

Both α-Pu and gallium stabilized δ-Pu undergo the same chemical reactions with oxygen, nitrogen and hydrogen, but with different rates. One of the critical attributes of the δ–Pu alloy was an oxidation rate that was much slower than for unalloyed α-Pu at room temperature. Despite slower reaction rates for δ–Pu, lengthy storage periods still may result in material surface conditions of concern when exposed to certain storage environments. For extended storage of plutonium following the end of the Cold War, conversion of excess Pu metal to Pu dioxide has become a desirable process due to long term stability of Pu in dioxide form when isolated from a few materials (e.g., water and organics). Reaction of Pu metal, while in storage, may lead to unstable surface hydrides or nitrides if organics and/or moisture are present with the Pu metal during storage.

Pu hydrides are formed on the surface of the Pu metal when hydrogen is made available in an oxygen limited storage condition. The complex reaction of Pu metal in an oxygen limited environment results in surface hydrides when moisture reacts with the metal and oxide layer to produce hydrogen which is then combined to form the surface hydride. The quantity of hydride produced is dependent on the quantity of hydrogen available from moisture or organic materials. Regardless of the amount produced, the Pu hydride is normally pyrophoric in room temperature air, where the hydride will react readily with the air to produce Pu dioxide, hydrogen and large amounts of heat. Heating of the metal piece occurs with the potential of reaching 500°C where the metal would spontaneously ignite, and potentially melt. For this reason, the handling of partially hydrided metal should take place in a moisture and oxygen free atmosphere to avoid undesirable reactions.

Plutonium hydride also reacts with nitrogen, or nitrogen in air to catalyze a reaction with both nitrogen and oxygen to form plutonium nitride (PuN) and hydrogen gas. The simultaneous reaction of the Pu hydride with nitrogen and oxygen releases 3.7 kJ of heat per gram of hydride which could also cause the bulk metal to overheat and spontaneously ignite [3]. Pu hydride and nitrogen essentially don't react until temperatures reach 200-250°C, at which point they react readily. It has been determined that when air reacts with Pu hydride, the heat produced by oxidation is sufficient to begin the Pu metal reaction with nitrogen. The simultaneous oxygen and nitrogen reactions catalyze a reaction that continuously forms hydride at the hydride-metal interface. The overall result is a very rapid consumption of hydride coated material in air, where a thickness of 1mm will be completely converted to corrosion products in approximately 1.5 minutes.

One example of the Pu hydride-nitride-oxygen reaction discussed above, was experienced at the Los Alamos National Laboratory when a Pu metal storage container was placed in a <3% oxygen glovebox after a worker was contaminated handling the container. The Pu metal had been placed in a metal cylinder, lid welded, welded cylinder placed in a plastic bag for glovebox removal, and then the plastic bag covered cylinder placed inside a steel slip-lid container sealed with tape around the lid-can interface. It was determined that the weld for the cylinder cap was initially defective, and over time, atmospheric pressure and temperature gradients caused Pu oxide particle formation and passage through the failed weld to the plastic bag interior. Radiolysis of the plastic bag generated hydrogen which moved inside the cylinder to the Pu metal, and conversion of the Pu metal surface oxide via auto-reduction to higher level very reactive oxides resulted in formation of Pu surface hydride when exposed to the hydrogen generated by radiolysis of the plastic bag. While in storage, the bag failed due to radiolysis, which permitted Pu oxide particles to be dispersed to the slip lid can and eventually contaminate the worker when the container was flexed during handling. After movement to a glovebox, and opening of the outer slip lid container, excess nitrogen and oxygen were made available to contact the Pu metal resulting in the hydride catalyzed reaction. Rapid corrosion of the Pu metal, with volume expansion to the lower density (11.5 g/cc) oxide, resulted from the combined nitrogen and oxygen exposure. The metal cylinder expanded to 150% of the original diameter to accommodate the oxide. The enormous volume expansion resulted in complete failure of the weld. Upon placement of the containers and material in an argon atmosphere glovebox, the catalyzed reaction stopped. The lessons learned from this example helped form the basis for the safe storage conditions for plutonium as detailed in DOE-STD-3013 [7] where moisture and organics are removed from the long term storage scheme.

Though publicly accessible data does not exist for confirmation, storage of Pu metal in oil of an organic base (e.g., not silicone oil), assumed to prevent oxidation corrosion of the metal, would produce the same concerns resulting from Pu interaction with plastic. The generation of hydrogen due to alpha particle interaction with the oil, auto-reduction of the submersed original oxide surface, and potential hydride formation are all possible. Though a search for literature related to Pu metal storage in oil or other organic liquids was unsuccessful, an example of Pu oxide stored with organic die lubricants that resulted in a storage container failure by gas generation was found [13]. While not a direct correlation, it is expected that an alpha particle from oxide or metal Pu has similar potential radiolysis implications for organic materials. Therefore, any Pu metal stored in liquid organic compounds like oil should be moved to an oxygen and moisture free atmosphere, and exposure to an oxygen environment only considered after adequate precautions are taken to prevent or mitigate uncontrolled rapid oxidation of the surface.

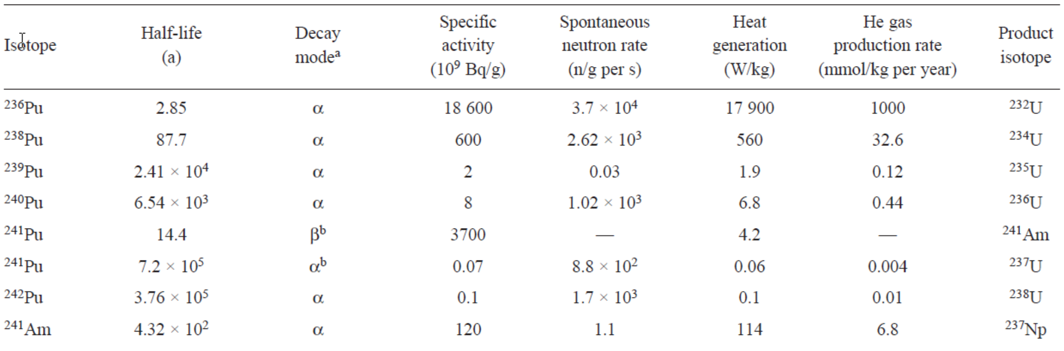
While the reactivity of Pu metal may be utilized for rapid conversion to another form (e.g., oxide), the catalyzing functions of elements, tremendous heats of reaction, and the ignition of bulk metal at fairly low temperatures must be considered to ensure a controllable reaction rate. Reaction products that include flammable/ignitable gases like hydrogen introduce additional considerations when trying to contain the readily dispersible reaction products. Despite the challenges associated with these reactions, processes have been developed for prompt Pu metal conversion that utilize the accelerated rates achievable by Pu hydride reactions [8,9,10].

In regard to long-term storage effects, Pu experiences damage from self-irradiation, or the radioactive decay of its nucleus. Decay results in lattice structure damage and transmutation products, which include helium and other actinides. Material properties of a Pu metal piece will be decay dependent, and the physical condition of the metal may also change over a long period. One phenomena postulated for Pu metal in extended storage is radiation induced cracking and warping that may result in pyrophoric surface behavior when the metal is reintroduced to an oxygen environment. For metal stored in sealed containers, this is a concern based on long term auto-reduction of Pu dioxide to reactive higher order surface oxides, as the metal reaches an equilibrium oxidation level inside the oxygen limited container. Cracking or warping of the metal piece by radiation induced void swelling, would result in fresh metal surface exposure. Redistribution of oxygen to the new metal surface area would increase the quantity of highly reactive surface oxides as the original dioxide PuO_2 layer was diluted further into Pu_2O_3 by auto-reduction. The current U.S. storage experience information base for Pu, has shown no examples where radioactive decay has resulted in a degraded condition of the metal with storage times of up to 40 years [12]. The heat generated during decay has been postulated to serve as a mechanism of significant metal self-annealing and lattice structure healing. While 40 years of storage experience has resulted in negligible metal physical degradation, the common belief among plutonium scientists is that visible damage will occur after a longer nucleation period, with rapid damage accumulation after that point. It is assumed that opening of metal stored over a long period of time in an inert atmosphere, with subsequent slow oxygen exposure, is an approach of easily dealing with radiation degraded metal prior to oxidation.

1.4 Isotope Composition Effects [3,11]

Plutonium is produced in reactors as a result of initial neutron capture by Uranium, U238, to produce U239, which beta decays first to Neptunium, Np239, and then to Pu239. Higher Pu isotopes are formed by additional neutron capture. Isotopic production essentially terminates at Pu242 because the half-life of Pu243 is only 5 hours. Table 3 lists nuclear data specific to the isotopes commonly present with Pu, including the results of radioactive decay to be expected after long term storage of a particular isotopic composition. Radioactive decay of Pu results in shielding, contamination and potential gas generation concerns that are dependent on the isotopic composition of the Pu. For reactivity considerations when considering oxidation, decay heat, may result in a significantly elevated metal temperature for massive metal pieces unless cooling methods have been employed. Oxidation reaction rates for Pu metal increase with temperature, and decay heat would result in an elevated temperature for bulk metal. Knowledge of typical isotopic compositions for various metal types (e.g., weapons grade, fuel grade, reactor grade) may help determine potential decay heat effects. Typically, weapons grade Pu contains up to 6% Pu240, fuel grade Pu has 6%-12% Pu240 with up to 1% Am241, and Reactor grade Pu has 12-25% Pu240 with up to 1% Am241. Based on the large decay heat values of Pu240 and Am241, fuel or reactor grade Pu metal that has been in storage for an extended period of time is most likely to exhibit elevated temperatures, and bears special consideration related to atmosphere exposure and oxidation processing.

Table 3: Nuclear properties of plutonium and related isotopes [3]



Isotope	Half-life (a)	Decay mode^a	Specific activity (10^9 Bq/g)	Spontaneous neutron rate (n/g per s)	Heat generation (W/kg)	He gas production rate (mmol/kg per year)	Product isotope
^{236}Pu	2.85	α	18 600	3.7×10^4	17 900	1000	^{232}U
^{238}Pu	87.7	α	600	2.62×10^3	560	32.6	^{234}U
^{239}Pu	2.41×10^4	α	2	0.03	1.9	0.12	^{235}U
^{240}Pu	6.54×10^3	α	8	1.02×10^3	6.8	0.44	^{236}U
^{241}Pu	14.4	β^b	3700	—	4.2	—	^{241}Am
^{241}Pu	7.2×10^5	α^b	0.07	8.8×10^2	0.06	0.004	^{237}U
^{242}Pu	3.76×10^5	α	0.1	1.7×10^3	0.1	0.01	^{238}U
^{241}Am	4.32×10^2	α	120	1.1	114	6.8	^{237}Np

2.0 CONVERSION OF PLUTONIUM METAL TO OXIDES

Conversion of plutonium metal into oxide is desirable for many reasons; including generation of Pu based nuclear fuel, elimination of reactive or pyrophoric material for transportation, and to meet nonproliferation goals. The experience of processing, handling and storage of Pu metal over >40 years has led to the development of practices to manage potential reactive behavior of plutonium materials and development of controlled thermal treatment and packaging steps. For stable long-term storage, oxide is the desired Pu compound because once fully oxidized to PuO2, the oxide is a chemically inert powder, insensitive to self-radiation damage, and it does not deteriorate. However, the oxide powder is very fine, and easily dispersed. The primary concern for oxide is absorption of moisture which will be decomposed by alpha radiation to generate hydrogen and oxygen gases that may over-pressurize containers, or exist in an explosive or flammable mixture that could disperse the Pu oxide if an ignition source were present. To avoid potential moisture induced gas generation problems, the post-oxidation steps for thermal treatment and packaging have been well defined [7]. However, for Pu metal, the initial conversion step to obtain oxide has many potential safety considerations since a standard similar to that for obtaining stabilized oxide doesn’t exist and/or has not been necessary. The following discussion covers various aspects of Pu metal conversion to oxide that require consideration when developing a metal oxidation approach. Much of the current state-of-the-art oxidation literature has resulted from the principal or joint research published by Haschke at U.S. DOE’s Los Alamos National Laboratory (LANL). Numerous alternate author publications exist, related to very specific oxidation mechanisms of various Pu materials, but for the the following sections, discussion is limited to the oxidation of either α-Pu or gallium stabilized δ-Pu, for which DOE at LANL has developed a definitive reference data set [5].

2.1 Metal Condition Effects on Oxidation Rate

Some conditions of Pu metal will result in a reaction where heating due to oxidation accelerates the reaction rate to the point where ignition of the metal may occur. The presence of a thin layer of PuO_2 on the surface will prevent pyrophoric behavior for temperatures up to approximately 500ºC for larger (e.g., not powder, chips, turnings or briquettes) pieces of metal. The initiation of pyrophoric behavior of surface oxidized plutonium metal with air depends on the metal thickness and temperature. Spontaneous ignition of Pu metal chips (less than 0.05 mm thick) and powders will occur when heated to 150–250°C in an oxidizing environment due to the presence of a pyrophoric Pu_2O_3 layer at the metal-oxide surface that heats the interior metal above the 500°C ignition point. Larger metal pieces, when the surface includes a thin layer of protective oxide will not ignite and burn unless heated to temperatures near ~500°C. The presence of a surface layer of protective oxide will invariably be the surface condition of Pu metal when allowed to sit in a room temperature dry oxidizing environment for a reasonable length of time (e.g., several hours).

In regard to differences in oxidation for different phases of Pu metal, the room temperature oxidation rate of α-Pu greatly exceeds that of gallium stabilized δ-Pu for temperatures below 400 ºC. However, the oxidation rates in either dry or moist air converge at approximately 400ºC as shown in Figure 3, and continue to share the same oxidation behavior at higher temperatures including the ~500ºC ignition point and beyond. This result is significant, as any effort to optimize a Pu metal oxidation process can use one procedure to address both α-Pu and gallium stabilized δ-Pu. Where only α-Pu is to be oxidized, the figure also shows how moisture catalyzed corrosion can be used to develop an approach to oxidize α-Pu proximate to the low temperature of 110ºC. Differences in rates of oxidation for the intermediate temperature Pu metal allotropes/phases are not discussed, as the Figure 3 data for unalloyed Pu accounts for phase transformations over the temperature range.

The alloy composition of Pu metal will impact the rate of oxidation, and also the melting point. For purposes of this document, only the gallium stabilized δ-Pu is discussed, as this is the most likely Pu alloy to be encountered based on preferable properties generated during alloying. If other Pu metal alloys are to be oxidized, special concerns like increased neutron emission at elevated temperatures for Pu-Al alloys, will exist. Examination of material phase diagrams is suggested to determine how melting point is impacted, and if any eutectics exist.

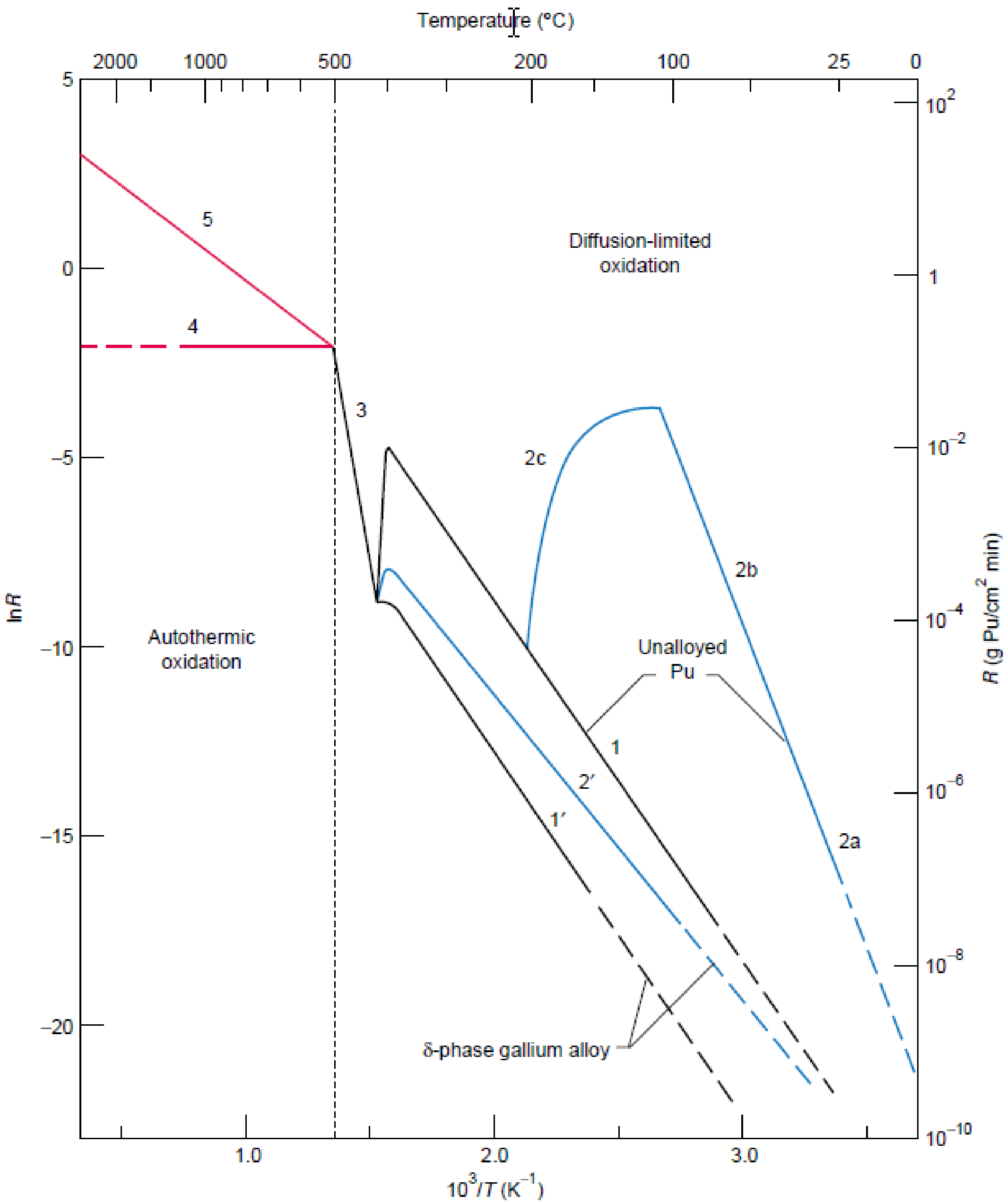
As discussed in section 1.4, the isotopic composition of the Pu metal may result in elevated temperature of the bulk metal due to decay heat. Other than these increased temperature effects, it is unlikely that variations in isotopic composition will produce a significant change in the oxidation rate for bulk metal. The isotope independent properties of crystal structure, and adherence of the generated oxide are the primary rate affecting properties for Pu metal.

2.2 Considerations for Heating with Oxidation [5]

2.2.1 Oxidation Rate Control

In the absence of catalyzing surface compounds the reaction of low specific surface area (e.g., <1 cm^2/g with mass typically >1g) pieces of α-Pu and δ-Pu metal with dry air (e.g., <5ppm water) is slow at room temperature. The oxidation rate depends on a number of factors which include temperature, exposed surface area, oxygen concentration, the quantity of moisture or other reactive vapors in the air, alloying, and the adherence of any protective or reaction limiting layer on the metal surface. Pu oxidation rates increase as the first four factors increase, and change variably as the other factors change. Since heating is the easiest of these factors to control in processing, Pu metal is typically oxidized by heating it in a furnace with an oxidizing atmosphere. When Pu metal is heated as part of an oxidation processing step, avoiding auto-ignition behavior at ~500ºC is important to ensure control of the oxidation reaction and to avoid generation of highly reactive molten Pu metal. While it may be desirable to have the oxidation reaction occur at a maximum rate, strict control of oxygen supply to the reaction, or heat removal from the reaction, is critical to maintain process control and to prevent auto-ignition of the Pu metal. Control of the reaction rate may be achieved using a furnace with atmosphere composition control to limit oxygen, or the temperature may be limited to a value significantly below that where eutectic formation or auto-ignition may occur.

For temperatures below ~500ºC, alloys of Pu will have different oxidation rates with primary rate dependence being related to the alloying element, and characteristics of the oxide formed. As an example of alloy impact on oxidation rate, Figure 3 shows that gallium stabilized δ-Pu must be heated to temperatures well above those required by α-Pu to realize the same oxidation rate. This rate difference can be explained by both oxidation mechanism and the characteristics of the oxide



Data on the steady-state oxidation rates of alloyed and unalloyed plutonium are summarized for a wide temperature range. Each labeled curve is an Arrhenius plot, showing the natural logarithm (ln) of the reaction rate R versus 1/T for a metal or alloy in a specific atmosphere or under a specific condition. The slope of each curve is proportional to the activation energy for the corrosion reaction. Curve 1 plots the well-known oxidation rate of unalloyed plutonium in dry air or dry O_2 at a pressure of 0.21 bar. Curve 2a shows the increase in the oxidation rate when unalloyed metal is exposed to water vapor at equilibrium pressures up to 0.21 bar (160 torr), a concentration equal to the partial pressure of oxygen in air. Curves 2b and 2c show the moisture-enhanced oxidation rate at a water vapor pressure of 0.21 bar (160 torr) in the temperature ranges of 61°C–110°C and 110°C–200°C, respectively. Curves *1′* and *2′* give the oxidation rates for the δ-phase gallium-stabilized alloy in dry air and moist air (water vapor pressure ≤0.21 bar), respectively. Curve 3 indicates behavior in the transition region between the convergence of rates at 400°C and the onset of the autothermic reaction at 500°C. Curve 4 defines the temperature-independent reaction rate of ignited metal or alloy under static conditions. The rate is fixed by diffusion through an O_2-depleted boundary layer of N_2 at the gas-solid interface. Curve 5 shows the temperature-dependent oxidation rate of ignited droplets of metal or alloy during free fall in air.

Figure 3. Arrhenius Curves for Oxidation of Unalloyed Plutonium in Dry Air and Water Vapor [5]

generated by the two different metals. Diffusion of oxygen to the metal-oxide reaction layer through the oxide adhering to the metal surface is the rate limiting aspect of oxidation at temperatures up to ~400ºC for both α-Pu and δ-Pu. As shown in Figure 3 at 400ºC, the oxidation rate curves converge based on temperature only dependence. Data beyond the 500ºC auto-ignition temperature is not available or relevant due to the loss of reaction rate control. It should be noted that the oxidation rate data from Figure 3 is a function of the surface area that is oxidizing. Surface area, in the absence of increasing surface roughness, decreases along with particle size during oxidation. The oxidation rate will also generally decrease with the reacting surface area of the object and a variety of other factors.

Oxidation of plutonium metal at or beyond the ignition temperature results in a process that is very similar, in both appearance and the associated fine ash product, to that of burning charcoal briquettes. For a static oxidation process, where the oxide product is not removed from the metal, the oxide layer will accumulate around a metal piece, and eventually result in reduced oxygen levels at the reacting oxide-metal layer with a corresponding reduced oxidation rate. Given enough oxide ash, the oxidation process may be completely smothered. Since the oxidation rate is surface area dependent, prior to reaching pyrophoric size, small pieces require more time to oxidize as the metal portion shrinks, but small piece oxidation is also more easily smothered by the oxide ash. For this reason, sorting of metal from ash by screening or raking is a standard step in Pu-metal furnace static oxidation processes. This step is performed to minimize oxidation time, expose fresh metal and ensure complete oxidation. The time required for a furnace to cool, separating oxide from metal, reheating the furnace, and repeating these steps in an iterative sequence can be extensive, and would result in a slow overall oxidation rate when determined in the context of the entire oxidation process.

For α-Pu, unique moisture enhanced oxidation behavior exists that may be advantageous when designing an oxidation process. Oxygen and moisture are usually present in Pu metal processing enclosures (e.g., gloveboxes) due to diffusion through gloves, ports or similar enclosure opening covers. As shown in Figure 3, water vapor accelerates oxidation by reacting directly with Pu metal. The reaction of α-Pu with moisture occurs at a much more rapid rate than pure oxygen at temperatures between –25°C and 200°C, and alters the oxidation rate in air at concentrations as low as one part per million. Hydrogen formed by Pu metal reacting with moisture can catalytically recombine with oxygen on the reacting metal surface to increase the oxidation rate to more than a hundred times higher for humid air than in dry air at room temperature. This ambient temperature accelerated oxidation rate is the primary reason plutonium metal has been handled in dry atmospheres (e.g., –40°C dew point or <5ppm moisture). Nitrogen or argon atmosphere enclosures, with <5% oxygen, are effective in reducing the oxidation of plutonium if water vapor is also excluded. However, if 1.3% moisture (50% relative humidity at standard temperature and pressure) accompanies the oxygen, rapid metal oxidation can be anticipated. For processing of unalloyed Pu only, moisture enhanced oxidation may be a viable option to using the higher temperatures required for gallium alloyed δ-Pu processing, as the accelerated rate at much lower temperatures will eliminate any potential problems related to Pu metal ignition and melting.

2.2.2 Oxide Formation and Collection

Differences in oxide formation on α-Pu and gallium stabilized δ-Pu are the primary cause of slower oxidation rates for δ-Pu at temperatures below 400ºC where oxygen diffusion through the adherent oxide layer governs the oxidation rate. At these temperatures, α-Pu, generally has a brittle crystal structure. In addition, α-Pu has significant variations between density of the 19.86g/cc metal, and 11.4 g/cc oxide, which results in increasing stress as the surface oxide layer grows in thickness. After reaching a critical thickness, the stress in the oxide causes pieces to crack and fall away from the metal, or spall. Assuming the oxide pieces are free to move away from the metal mass, reduced time will be required for oxygen diffusion through the thinner oxide layer at the spall location. The brittle crystal structure of the α-Pu favors spalling behavior as a method of stress relief due to volume expansion during conversion from 19.86 g/cc metal to 11.4 g/cc oxide. In contrast, the gallium stabilized δ-Pu has a ductile crystal structure, a metal density of 15.4 g/cc, and the same α-Pu oxide density of 11.4 g/cc. The result of these differences is that the oxide produced for the δ-Pu is adherent at lower temperatures, protective, and does not spall as readily as for α-Pu due to stress accumulation as the oxide layer grows. Therefore, the steady state oxidation rate for δ-Pu lags that of α-Pu due to more time required for oxygen to diffuse through the a generally thicker oxide layer. This lag only occurs below 400ºC, where diffusion governs the oxidation rate.

For either α-Pu or δ-Pu alloy, the oxidation product has a typical particle size of <5µm. If the ash oxide product is not removed from the metal during oxidation, the accumulating layer will result in reduced oxygen availability at the reacting oxide-metal surface which impedes oxidation. For reasonable oxidation procedure cycle times, it will likely be necessary to include steps to separate oxide and metal. Since the oxidation time for pieces increases as particle size, and surface area, decreases, sifting, screening or sieving of the oxidized product is also required to ensure complete oxidation of all metal, or to determine when oxidation is complete (e.g., remaining metal pieces are all smaller than a critical size). The adherent oxide present for processing δ-Pu may result in extensive processing times. Consideration of δ-Pu metal piece size reduction to increase the initial surface area, or a method of agitation during oxidation to enhance removal of the oxide may be desirable to minimize processing time.

While overlying oxide thickness or alternate Pu alloying may affect the oxidation rate, the following example is presented as an application of the Figure 3 information for a 2 Kg sphere of either α-Pu or δ-Pu. Assumptions for this example include temperature control at ~460ºC, and adequate oxygen supply to the reacting surface. Since a sphere has the lowest surface area to mass ratio for any geometry, it will be used to establish the upper bound of expected oxidation time. Oxidation is assumed to be complete when the remaining metal nugget reaches a diameter of 3 mm, with justification for this 3 mm dimension provided in a later section. The oxidation time calculation (neglecting time for oxide separation from metal) is based on the following information:
Spherical Mass, M=2000 g
Pu density, ρ= 19.86 g/cc(α), 15.7 g/cc (δ)
Spherical Volume, $V= \pi D^3/6=M/\rho$=100.7 cc (α), 127.4 cc(δ)
Diameter, $D=(6V/\pi)^{1/3}$, D=5.77 cm (α), 6.24 cm (δ)
From Figure 3, R=0.018 g Pu/cm^2-min for either α-Pu or δ-Pu at T~460ºC
Note that a similar oxidation rate may be obtained for moist air with α-Pu at T~100ºC.

Table 4 lists several intermediate step results for converting the metal mass to oxide over time, reducing the diameter to adjust the metal surface area, and recalculating the oxide and new metal diameter produced until the endpoint of 3 mm (0.3 cm) is reached. From the results, it is seen that the difference in densities contribute to a slightly longer oxidation time for δ-Pu, but in relation to the total oxidation time, which neglects heat-up, cool-down and any oxidation removal steps, the difference will be a small percentage of the total time required to oxidize a massive piece of Pu metal. From the table, the benefit of piece size reduction to maximize surface area is evident.

Table 4: Oxidation Time for 2 Kg Pieces of α-Pu and δ-Pu

Time (Hr)	Remaining Pu Metal Mass (g)	α-Pu Diameter (cm)	δ-Pu Diameter (cm)
0	2000.00	5.77	6.24
10.6	1028.42	4.62	5.00
19.1	525.79	3.70	4.00
27.6	222.12	2.77	3.00
36.1	65.78	1.85	2.00
44.5	8.24	0.93	1.00
50.3	0.28	0.30	0.32
50.5	0.22	0.28	0.30

2.2.3 Furnace Design

Extensive experience with static oxidation of Pu metal exists from nuclear material development programs. Critical furnace design parameters include the heating temperature, temperature control, oxidation atmosphere control, Pu oxide dusting control (e.g, limit airflow to minimize dust movement), and materials of construction selected to withstand exposure to any gases generated during oxidation. Where oxidation process time is to be minimized, it is also advantageous to have expedited cooling of the furnace contents to facilitate prompt separation of oxide from metal during processing. Ideally, a minimum particle size (e.g., 3mm) would be selected to determine when the oxidation process was complete. After metal surface stability been confirmed, metal pieces would then be placed on a screen that would retain all metal larger than the critical size, oxidation performed, and agitation of the metal over the screen with a catch-basin or tray under the screen to collect the oxide. After separating the oxide from metal, the oxidize-cool-separate sequence would be repeated until no Pu metal pieces remained on the screen. Another furnace consideration is that placement in an inert gas may result in electrical performance problems. While electrical devices perform properly in nitrogen gas, they are known to have conductor arcing problems in argon gas.

Based on the adherent δ-Pu oxide, and the tendency of static oxidation to result in smothering of the reaction, furnaces with mechanical agitation functions to encourage oxide spalling, remove oxide from metal, and collect the oxide have been suggested for production applications where large quantities of δ-Pu metal need conversion to oxide (e.g., weapons grade δ-Pu MOX fuel production per treaties between U.S. and Russia). Furnaces that implement dynamic excitation of the oxidizing material are not yet fully mature technology for plutonium processing. Excluding production type applications, where large quantities of Pu metal require oxidation, static heating methods with strict temperature and oxygen control are recommended to avoid metal ignition. The temperatures of plutonium fires usually exceed the melting point of plutonium (640°C) and may cause unreacted metal to consolidate into a molten configuration, that may bond with or breach containment, pans or holders. These potential problems, justify the much slower, but controllable process of <500ºC furnace static oxidation.

Additional furnace design attributes that should be considered during process design include sizing of material containers or holders to accommodate the volume expansion of the Pu metal as it is converted to oxide, retort material of construction, and ventilation system filtering and material selection that accounts for filtering of small oxide particles along with potentially corrosive off-gases or evolved species that may attack the ventilation path materials. The following sections cover detailed evaluation of some typical furnace design considerations for Pu metal oxidation. The information listed is limited to oxidation of pure or gallium alloyed Pu metal, and does not assume the composition of any impurities present in or on the metal. Other Pu metal alloys may have unique considerations based on interaction with system materials of construction. It should be noted that complex Pu alloys or mixtures have usually been considered for conversion via dissolution rather than oxidation, and dissolution may be required if the species evolved during oxidation present containment, personnel shielding, or other problems.

2.2.3.1 Pu Metal Volume Expansion

The simplest way to account for Pu metal volume expansion in the furnace design is to put a volume or mass limit on the pieces of Pu metal that will be oxidized. For δ-Pu this, along with piece size reduction, will have an additional benefit of minimizing the number of times oxide needs to be separated from the metal. Using the maximum theoretical metal density of 19.86 g/cc for α-Pu metal, and a conservative bulk density value of 2.5 g/cc for Pu oxide, a minimum volume expansion factor of 8 should be used to determine containment volume for the resulting oxide. If regular separation of oxide from metal is included as part of the oxidation process procedure, smaller containment volumes may be used.

2.2.3.2 Furnace Retort Material Selection

It is assumed that furnace static oxidation will permit the use of an inert containment or catch pan to address the unlikely event of molten Pu metal. With eutectic formation eliminated as a concern, the furnace retort material should be selected with consideration of potential corrosive off-gases if metal impurities exist that will be evolved during oxidation in the form of a corrosive gas (e.g., HCl gas), or condense as a molten salt (e.g., $CaCl_2$). Since the furnace will be operated with an oxidizing environment at all times, the oxide layer on the retort should be selected to avoid unacceptable corrosion for temperatures in excess of maximum value regularly used for oxidation.

The use of a high Nickel-Chromium alloy is recommended for the furnace retort. Based on the high melting point temperature of aluminum and chromium-plutonium alloys, high temperature materials that result in a tenacious, or closely bound, alumina or chromia surface oxide are preferred for the retort material. Table 5 includes several alloys recommended for temperatures <900°C applications that generate a tenacious surface oxide. Any of the alloys listed in Table 5 would be excellent retort materials if pure metal was being processed for temperatures <500°C. However, the high molybdenum content of Inconel-625 would result in much better corrosion resistance if impure metals were expected to be processed for temperatures below 900°C due to both material strength and oxidation resistance.

Table 5: High Temperature Oxidation Resistant Alloys

	Alloy Element % (Nominal)													
Alloy (UNS#)	Ni	Cr	Fe	Si	Mn	C	Al	Mo	Ti	Cb	Zr	Y	Co	W
I-625 (N06625)	61	21.5	4	0.1	0.1	0.05	0.4	9	0.4	3.6				
I-693 (N06693)	60.5	29	3.5	0.2	0.2	0.02	3		0.4	0.6				
VDM 602CA (N06025)	63	25	9.5			0.20	2				0.08	0.1		
RA-333 (N06333)	45	25	18	1		0.05		3					3	3

2.2.3.3 Gallium Alloy Effects for δ-Pu

Gallium, as the typical δ-Pu stabilizing alloying element, has a few potential furnace retort and ventilation material of construction interaction considerations. The information in this section is provided as an example of material assessment in case processing of Pu metal alloyed with elements other than gallium, or having surface impurities, results in similar or other unique interaction effects when designing containment and ventilation for a metal oxidation process system.

Gallium oxide, generated as a result of the oxidation of Pu-metal alloyed with up to 1% Gallium, is present as Ga_2O_3 in PuO_2-1 wt% Ga_2O_3 [14]. The gallium oxide is not volatile, but in gaseous form will attack certain metals. Even in a high temperature reducing environment, nickel alloys (e.g. Inconel-625) have been shown to be compatible with the evolved gallium [15]. For a predominantly oxidizing environment, similar to what would be expected in an oxidation or stabilization furnace, the absence of gallium in the off-gas would permit the use of either nickel or stainless steel alloys without concern related to gaseous gallium oxide attack.

For the alloying elements listed in Table 5, there are no published incidents of Gallium induced Liquid Metal Embrittlement (LME). However, severe embrittlement occurs when aluminum is wetted by liquid gallium. The primary condition required to cause LME is intimate contact between an embrittling liquid & metal surface [16]. Based on the anticipated furnace static oxidation process and environmental conditions, metallic component embrittlement due to contact with liquid metal gallium is not expected, as the furnace oxidizing environment would establish a layer of oxide on metal surfaces that would protect the metal from embrittlement. For standard operations, where maximum temperature is set to be <500°C, Pu-Ga metal will not ever reach temperatures sufficient to cause melting and LME.

Similar to the LME type of failure, Solid-Metal Induced Embrittlement (SMIE) occurs for interaction between two materials at temperatures below the melt point of the embrittlement causing element. However, SMIE has only been known to occur in LME couples, and, as such, is considered a prerequisite for SMIE. Since intimate contact between two solids is required for SMIE, a refractory material pan or boat preventing prolonged metal to metal contact would be sufficient defense against SMIE.

2.2.4 Material Containment Methods

While a furnace static oxidation process should be designed to prevent ignition and melting of Pu metal, the process system should still be designed to mitigate any incident where ignition and melting might occur (e.g, controller failure, or runaway heater). The simplest way to mitigate a melting or ignition event is to use a containment pan that, can contain the molten volume, and won't react with molten or hot Pu metal. This step alone will eliminate the need to consider eutectic formation between molten Pu metal with additional layers of containment like the furnace retort and glovebox shell.

During early nuclear material development work, slightly oxidized tantalum was found to be quite unreactive with molten plutonium and led to the development of reusable foundry hardware. However, in an elevated temperature oxidizing environment, the tantalum would continuously oxidize and degrade similar to the Pu metal. Therefore, numerous furnace runs would exclude tantalum as a practical containment vessel material. Calcium oxide, magnesia or alumina, are refractories that have both been used in plutonium oxidation applications. Ideally, the use of a refractory material boat, or Pu metal holder, placed inside a second refractory material pan would be used to provide two layers of containment in the event of molten Pu metal. All containment devices should be sized to accommodate the anticipated volume of oxide, with a geometry that will contain the volume of metal in liquid form. For an additional containment layer, an exterior furnace catch pan may be fabricated from refractory material, and placed under the furnace body.

2.2.5 Complete Oxidation Verification

Furnace static oxidation of Pu metal almost invariably results in oxide covered metal pieces despite the duration of the oxidation cycle. In addition, the length of time required to oxidize metal increases as the surface area decreases during oxidation as shown in section 2.2.2. For these reasons, it is prudent to determine a maximum particle size to use as the criterion for concluding that the metal oxidation step is complete. DOE-STD-3013 [7], Section A.6.1.1 states that particles with mass <1 gram, and specific surface area of <100 mm^2/g exhibit this undesirable behavior. The standard requirements were developed to avoid the potential instability associated with particles of this size when storage containers would be opened in the future. This same behavior, which is problematic for packaging, is desirable for complete oxidation of a Pu metal item. Since stabilization of the oxidation product will also likely be required, any metal particles that do not meet the limits of <1 gram & >100 mm^2/g are certain to be fully oxidized if subjected to DOE-STD-3013 stabilization requirements to generate a final Pu oxide product that is safe for transport and storage. For the oxidation product of small metal pieces, it is conservative to use a spherical geometry to obtain the maximum allowable product particle size from the mass and specific surface area limits. Additionally, the less dense delta-phase material would result in greater particle dimensions for calculations based on both mass and specific surface area calculations. For this reason, the dense α-Pu (19.86g/cc) will result in more conservative maximum product particle size in calculations. The following calculations determine the maximum allowable product particle size based on a maximum mass of 1 gram, and maximum specific surface area of 100 mm^2/g:

<u>Max Allowable Sphere Diameter for Particle Mass <1 gram:</u>
Mass (gram)=Density (g/cc) x Volume (cc)
$1\ g = 19.86 g/cc\ (\pi D^3/6)$
D=0.458 cm
Dmax<4.58mm

<u>Max Allowable Sphere Diameter for Specific Surface Area <100cm^2/g</u>
Specific Surface Area (mm^2/g)=Surface Area (mm^2)/Mass (g)
$SSA= (\pi D^2)/[(19.86g/cc \times 1cc/1000mm^3) \times (\pi D^3/6)]=6000/[19.86(D)]$

$100mm^2/g = 302/D$
D=3.02mm
Dmax<3.02mm

Therefore, the maximum allowable product particle size would be based on the ~3mm value obtained from the specific surface area calculation.

Separation of oxide from metal by raking, sifting, screening, or sieving of the product should be based on the 3mm dimension. It should be noted that the maximum particle size refers to the single smallest dimension of a metal piece (i.e. thickness of a thin disk instead of diameter), and sieving or screening of the oxidation product would ensure that a particle that exceeded this dimension would be retained for additional oxidation or size reduction.

Figure 4 presents an in-furnace retention option that could meet the containment expectations for an incident that may result in molten Pu metal, and also facilitate oxide removal and collection during the oxidation process. The placement of a grate or sieve under the oxidizing metal, though not previously demonstrated for Pu oxidation, would permit the Pu oxide to fall away from the metal and maximize the oxidation rate. If a sieve is used, retention of pieces >3mm may be ensured without requiring an ash sieving step at the completion of oxidation. The sieve will need to be fabricated from an elevated temperature oxidation resistant material to ensure that deterioration or failure does not occur during the anticipated duration of oxidation exposure.

2.2.6 Oxide Stabilization Considerations

The DOE-STD-3013 for stabilization of Pu oxide has been referenced in several of the previous sections. It is assumed that any metal subjected to oxidation to minimize reactivity will also be subjected to a stabilization step that converts all Pu oxide to the stable di-oxide form (e.g, no reactive sub-oxide present), minimizes moisture, and eliminates organic materials. If a stabilization step is planned to follow metal oxidation, there are a few considerations that will greatly simplify meeting requirements for the final stabilized material. Implementation of the following oxidation process design considerations will greatly improve the likelihood of successful material stabilization:

A. Oxidation of metal to 3mm or smaller pieces ensures, that even prior to stabilization, the material will meet size/geometry requirements necessary to ensure complete oxidation of ALL metal at the end of the stabilization step.
B. Oxidation and storage of the oxidation product in a dry environment will minimize the material moisture content prior to the stabilization treatment, and further ensure that the material will pass moisture evaluation limits after stabilization and storage in a similar dry environment.
C. Storage of the oxidation product in an oxygen rich environment will ensure that no reactive oxide formation occurs while any <3mm pieces of partially oxidized metal await stabilization. This should ensure repeatable heat cycles for the furnace due to minimization of any localized ignition behavior during stabilization.

2.2.7 Nuclear Safety Considerations

The hazards associated with Pu justify special safety considerations and controls to account for the fissile and unique reactive characteristics of the material. Oxidation and other corrosion reactions typically produce small particles containing plutonium and significantly increase the dispersal hazard posed by the material, but dispersal can be readily mitigated by most containment safety related control schemes. Standard safe plutonium handling methods encourage robust containment and ventilation systems to protect workers and the public [3]. Containment and ventilation design concepts for Pu processing are well defined in [3]. Both preventive and mitigative safety controls require consideration for eutectic formation, since melting of Pu metal may be caused by the oxidation process, outside heat sources like a facility fire, or opening a container of reactive metal in an environment conducive to rapid oxidation. In general, the following controls may be implemented to cover the Pu metal melting accident.

A. Open Pu metal storage containers in dry (dew point <-10ºC) inert (argon) environment.
B. Place magnesium oxide sand proximate to all metal handling steps in case of Pu fire.
C. Place Pu metal in double containment of refractory boat and pan at all times during handling and oxidation.
D. Limit maximum temperature of all processing steps to a value safely below auto-ignition temperature of Pu metal (<500ºC).

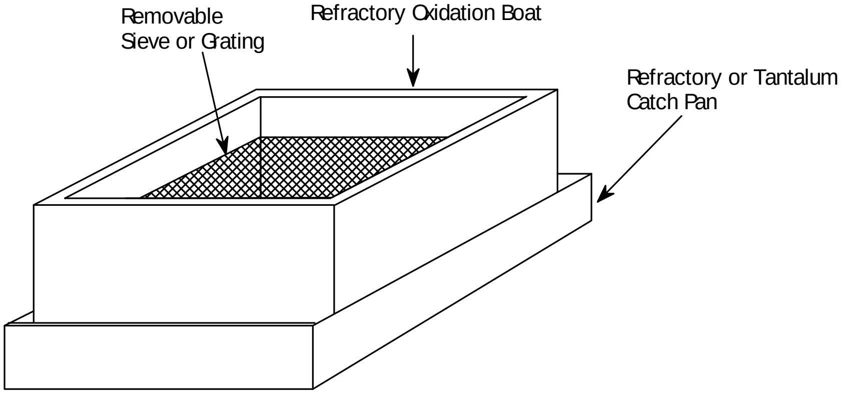


Figure 4. In-Furnace Pan/Boat

2.3 Oxidation Products

2.3.1 Oxide Characteristics [3]

As stated previously, the oxide formed by the oxidation of metal is ~5 μm in size for α-Pu, and tends to be even smaller for δ-Pu. In addition, Pu oxide is hygroscopic, or has an affinity for absorbing and adsorbing water from the surrounding atmosphere due to the high surface area of the small particles. For typical laboratory conditions, Pu oxide adsorbs water up to 1% of its weight, and up to several mass per cent in humid atmospheres. Adsorbed moisture can be removed by heating the oxide in air. A large fraction of the moisture acquired during air exposure is physically adsorbed and can be removed by heating at 50–100°C. Calcining at 700°C will result in residual moisture levels of less than 0.2 mass per cent. Heating to temperatures up to 1000°C is necessary to completely remove any remaining chemisorbed water. When PuO_2 is heated above 900°C, particle specific surface area is reduced below 5 m^2/g. This reduced surface area value limits re-adsorption of moisture to about 0.2% of the oxide weight in air at room temperature with 50% relative humidity. Reduction of the water content is desirable to minimize the potential for container pressurization due to gas generation, and also to diminish neutron moderation and the associated criticality risk.

2.3.2 Material Control & Accountability Considerations

Since the Pu metal will be changing form during the oxidation process, it is assumed that Material Control & Accountability (MC&A) design considerations will be utilized to ensure that the mass of fissile metal matches the mass of fissile material in the oxidized product. The accountability steps expected for processing a single container of metal are listed here:

1. Receive a single feed container with Pu metal from storage location.
2. Move container to a containment enclosure (e.g., inert/dry glovebox)
3. Remove all outer containers except one in contact with Pu metal.
4. Measure and record mass of container with metal on scale (MC&A Data)
5. Remove metal from the container and place in furnace containment.
6. Weigh empty container (MC&A Data)
7. Oxidize metal in furnace
8. Move oxide to a pre-weighed product container

9. Move product container to scale, and weigh (MC&A Data)
10. Remove product container from enclosure
11. Perform non-destructive assay to characterize distribution of isotopes (MC&A Data).

Therefore, the only MC&A equipment required inside the enclosure would be a calibrated scale for weighing the metal and oxide product. Since the material form changes during conversion from metal to oxide, additional measurements will likely be required to determine composition based on elemental weight percent, and the distribution of isotopes. More advanced assay equipment like a calorimeter, neutron multiplicity counter, and gamma isotopic system would be required to obtain this MC&A information.

2.3.3 Interim and Long Term Packaging

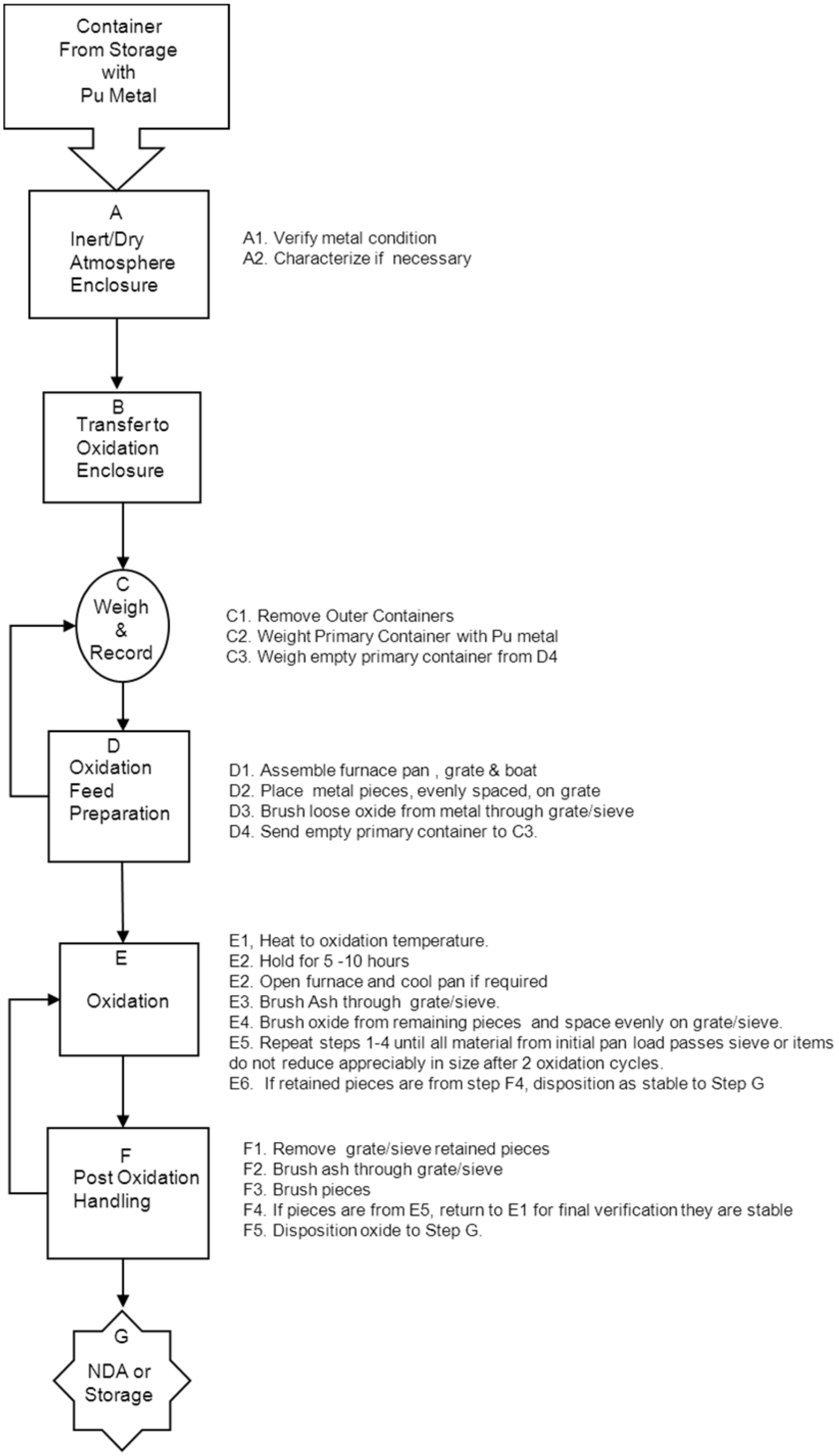
The oxidation product is still considered reactive based on the process described. Since the particle size used to conclude oxidation of a piece of metal was not selected as ~5µm, it can be assumed with surety that some small metal pieces remain unreacted. Depending on whether a stabilization step is planned for the oxidation product, and the delay time between the end of oxidation, and the beginning of stabilization, the following points should be considered:

1. Refrain from using packaging that has organics or moisture present to prevent gas generation (e.g., clean, dry metal containers).
2. Ensure oxide atmosphere has low moisture (<-10C dew point) to prevent adsorption/absorption of moisture and hydrogen gas generation.
3. Ensure atmosphere is oxidizing to prevent auto-reduction of dioxide on unreacted metal pieces.

For material where immediate stabilization is not practical, items 1 and 2 still warrant consideration. The uptake of moisture prior to stabilization will only require more moisture removal, and simply result in the potential for reduced success for a stabilization confirmation step like thermo-gravimetric analysis for moisture content.

3.0 OXIDATION PROCESS FLOWSHEET

Based on all of the considerations presented in this document, a system design may be developed to ensure safe/secure operation of a furnace static oxidation process. Figure 5 presents an example process flowsheet that may be followed to design and develop Pu metal oxidation processes and procedures. The flowsheet assumes that a sealed container of Pu metal will be introduced to a low-moisture, inert gas atmosphere enclosure for examination prior to processing. No assumptions are made in the flowsheet in regard to specific system equipment, other than the use of a furnace with gas atmosphere and temperature control. Steps related to removing or separating the oxide product from remaining metal may be eliminated if alternate, possibly dynamic mechanical methods are employed (e.g., intermittent impact or shaking of pan/boat without de-energizing furnace). Figure 6 is a more detailed description of blocks E and F in Figure 5. Any values listed in these flowsheets are approximate, and should be considered as good starting points during process proof testing.



A1. Verify metal condition
A2. Characterize if necessary

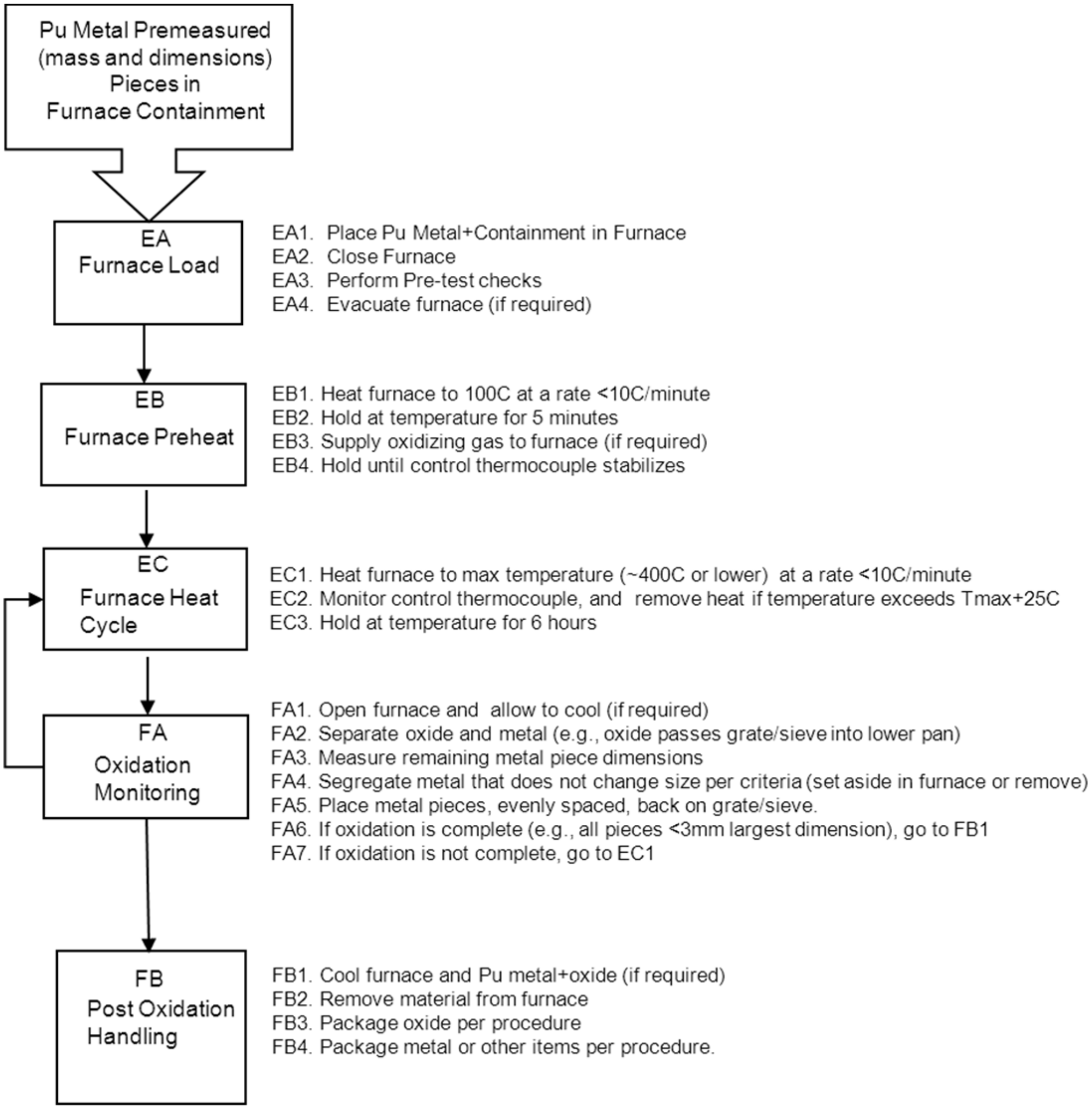
C1. Remove Outer Containers
C2. Weight Primary Container with Pu metal
C3. Weigh empty primary container from D4

D1. Assemble furnace pan , grate & boat
D2. Place metal pieces, evenly spaced, on grate
D3. Brush loose oxide from metal through grate/sieve
D4. Send empty primary container to C3.

E1, Heat to oxidation temperature.
E2. Hold for 5 -10 hours
E2. Open furnace and cool pan if required
E3. Brush Ash through grate/sieve.
E4. Brush oxide from remaining pieces and space evenly on grate/sieve.
E5. Repeat steps 1-4 until all material from initial pan load passes sieve or items do not reduce appreciably in size after 2 oxidation cycles.
E6. If retained pieces are from step F4, disposition as stable to Step G

F1. Remove grate/sieve retained pieces
F2. Brush ash through grate/sieve
F3. Brush pieces
F4. If pieces are from E5, return to E1 for final verification they are stable
F5. Disposition oxide to Step G.

Figure 5. Example Oxidation Process Flowsheet



EA1. Place Pu Metal+Containment in Furnace
EA2. Close Furnace
EA3. Perform Pre-test checks
EA4. Evacuate furnace (if required)

EB1. Heat furnace to 100C at a rate <10C/minute
EB2. Hold at temperature for 5 minutes
EB3. Supply oxidizing gas to furnace (if required)
EB4. Hold until control thermocouple stabilizes

EC1. Heat furnace to max temperature (~400C or lower) at a rate <10C/minute
EC2. Monitor control thermocouple, and remove heat if temperature exceeds Tmax+25C
EC3. Hold at temperature for 6 hours

FA1. Open furnace and allow to cool (if required)
FA2. Separate oxide and metal (e.g., oxide passes grate/sieve into lower pan)
FA3. Measure remaining metal piece dimensions
FA4. Segregate metal that does not change size per criteria (set aside in furnace or remove)
FA5. Place metal pieces, evenly spaced, back on grate/sieve.
FA6. If oxidation is complete (e.g., all pieces <3mm largest dimension), go to FB1
FA7. If oxidation is not complete, go to EC1

FB1. Cool furnace and Pu metal+oxide (if required)
FB2. Remove material from furnace
FB3. Package oxide per procedure
FB4. Package metal or other items per procedure.

Figure 6. Detailed Furnace Oxidation Steps

4.0 SUMMARY

The conversion of Pu metal to a stable oxide is simple in concept, but cumbersome in implementation. Strange physical behavior changes with temperature, major oxidation rate changes with alloying, spontaneous chemical reactions that may be difficult to control, and radioactivity all add to the complexity of developing an oxidation approach. Despite all of the potential problems associated with Pu metal oxidation, it is possible to develop very controlled process steps that will prevent the problems and permit the safe execution of the conversion of Pu metal to oxide. The following bullets summarize the critical steps required for any oxidation process which may be developed.

1. The process containment and facility should have ventilation system design consistent with amount of material at risk, and the ramifications of containment failure.
2. It is necessary to characterize reactivity of Pu metal in an inert environment prior to exposure to a reactive (5ppm or greater moisture, 3% or greater oxygen) atmosphere.
3. Exposure to an elevated temperature furnace oxidizing atmosphere requires strict temperature control.
4. The potential for material interactions caused by eutectic formation or metal melting should be accounted for in the process containment design.
5. The oxidation process should be designed so that it is conducted with Pu in multiple layers of containment under normal and accident conditions.
6. The minimum metal particle size criteria, or material stability criteria for items that will not oxidize, should be established to have measurable criteria for determining the end of the oxidation cycle.
7. Post oxidation handling methods (e.g., moisture and organic exposure minimization) that will facilitate any additional processing steps should be considered for implementation.

Consideration of these items during the development of a metal oxidation process for either α-Pu or gallium stabilized δ-Pu should lead to a rugged and safe process design. Oxidation of other Pu alloys would require additional considerations as detailed in section 2.0. Though plutonium, with extreme sensitivity to almost all perturbations in composition and meta-stability in almost all forms, may be considered a metallurgist's dream, that same sensitivity to small changes requires in-depth evaluation of any processing method. While this document cannot be claimed as exhaustive when evaluating a Pu metal oxidation method for potential problems, it contains reference to all currently known issues related to oxidation, that if considered, should result in a safe processing approach.

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