THE EFFECT OF ANNEALING ON THE REVERSAL OF AMORPHIZATION IN PLUTONIUM TETRAFLUORIDE

by

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STATEMENT OF DISSERTATION APPROVAL

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ABSTRACT

This dissertation is focused on the radiolysis of plutonium tetrafluoride under long-term storage conditions. Amorphous plutonium tetrafluoride samples were subjected to thermogravimetric/differential thermal analyses, X-ray diffraction analyses, and muffle furnace annealing experiments in argon gas to investigate the totality of this radiolysis, and the effect that thermal annealing has on its reordering. There are three main areas of focus presented in this work that were used to investigate these phenomena.

First, thermogravimetric/differential thermal analyses and X-ray diffraction analyses were used to uncover the possible mechanisms responsible for the amorphization in plutonium tetrafluoride through pre-annealing and post-annealing analyses on milligram samples. Second, gram samples of the plutonium tetrafluoride were annealed within flowing argon gas for short time durations. These samples were analyzed with X-ray diffraction to determine the rapidity of recrystallization in plutonium tetrafluoride. Third, gram samples of the plutonium tetrafluoride were annealed within flowing argon gas for long time durations. These samples were analyzed with X-ray diffraction to determine the effect of time at temperature on the recrystallization in plutonium tetrafluoride.

The results of these three investigations are that plutonium tetrafluoride that has been stored near 50 years is amorphous. Its amorphization appears to be a result of self-induced alpha radiolysis from the decay of the plutonium isotopes. The alpha particle and the recoil nucleus of this decay look to be the primary driver of this radiolysis through

Frenkel type defects and F-center formation. Radiolysis in plutonium tetrafluoride does not follow the crystal lattice parameter expansion as seen in plutonium dioxide. The crystallite size in amorphous plutonium tetrafluoride has been shown to increase under annealing conditions, and this recrystallization begins near 400°C under short and long time scales (minutes to hours) in argon gas.

I dedicate this dissertation to Debra DeSandre, the most beautiful person that I have ever known. I owe Debbie immensely for my success in this endeavor. She would not allow me to feel sorry for myself or give anything less than my best. I am so lucky to have lived life alongside her. Through her unwavering loyalty and belief in my ability to accomplish remarkable successes, she drove me to prosper in areas of life that I never thought possible. She wore a positive will and attitude that could not be bent through any means beyond her own and left a grand impression on all those who were lucky enough to know her. I miss her more than anything in my life, but I am so pleased to know that this dissertation has the life and the passions that we shared together poured into every word. I love you and thank you more than I can ever understand. This is for you, Debra.

“The only thing more expensive than education is ignorance” - Benjamin Franklin

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CHAPTER 1

INTRODUCTION

Plutonium is one of the most curious substances on earth. Plutonium is also one of the most difficult substances on earth to work with because of its status as a highly safeguarded material and as a toxic substance. Part of plutonium's mysterious nature lies in its tendency to self-damage over time. This self-damage is a result of alpha radiolysis from the internal radioactive decay of the given isotope to its progeny. The work presented here focuses on the effect that that self-induced radiolysis has on plutonium tetrafluoride stored for nearly 50 years, and the influence that thermal annealing has on the reversal of the crystal lattice structure damage caused by that self-radiolysis.

1.1 The behavior and value of plutonium

Each isotope of plutonium decays to a progeny isotope, but the plutonium 239 isotope is typically the most interesting from a safeguarding and value standpoint. The plutonium 238 isotope certainly has notoriety among the radioisotope generators, but plutonium 239 makes the best fissile ceramics and metals due to its high thermal neutron cross section and low spontaneous fission rate compared to the other isotopes of plutonium.

This is an interesting time to work with plutonium, as there has never been a time in history that plutonium has been stored for such long time periods. Therefore, there are new and interesting phenomena related to its behavior under long-term (>30 years) storage condition. There is limited information on the behavior of plutonium tetrafluoride due to its limited use in the civilian sector. Information on plutonium oxide is much more available as mixed-oxide fuel contains uranium and plutonium oxide, capable of being used in commercial nuclear power plants. However, with plutonium compounds becoming more precious as the years of ceased plutonium production increase, plutonium tetrafluoride compounds will need to be investigated for their long-term storage stability. Therefore, this work is focused on the early investigation of plutonium tetrafluoride under long-term storage conditions, the radiolytic damage that is inherit with plutonium and its effect on plutonium tetrafluoride, and the effect that thermal annealing has on the recrystallization of amorphous plutonium tetrafluoride.

1.2 Publications

There are three main areas of focus in this work, Chapters 2, 3, and 4. Chapters 2, 3, and 4 are comprised of journal articles submitted for publication. These papers encompass the bulk of work that was used to investigate the phenomena of radiolysis and annealing effects in plutonium tetrafluoride. The layout of this dissertation is as follows:

Chapter 1 is the introduction and justification for this work. Chapter 2 is focused on thermogravimetric/differential thermal analyses and X-ray diffraction analyses that were used to uncover the possible mechanisms responsible for the amorphization in plutonium tetrafluoride through pre-annealing and post-annealing analyses on milligram samples. Chapter 3 discusses the use of plutonium tetrafluoride on the gram scale to investigate the effect of thermal annealing within flowing argon gas for short time durations. Chapter 3 samples were analyzed with X-ray diffraction to determine the rapidity of recrystallization in plutonium tetrafluoride. Chapter 4 discusses the use of plutonium tetrafluoride on the gram scale to investigate the effect of annealing within flowing argon gas for long time durations. Chapter 4 samples were analyzed with X-ray diffraction to determine the effect of time at temperature on the recrystallization in plutonium tetrafluoride. Chapter 5 contains the Conclusion and Future Work.

CHAPTER 2

RADIOLYSIS AND CRYSTALLINITY IN PLUTONIUM TETRAFLUORIDE

2.1 Abstract

A sample of plutonium tetrafluoride that was separated prior to 1966 at the Hanford Site in Washington State was analyzed at the Pacific Northwest National Laboratory (PNNL) in 2015 and 2016. The plutonium tetrafluoride, as received, was an unusual color and considering the age of the plutonium, there were questions about the condition of the material. These questions had to be answered in order to determine the suitability of the material for future use or long-term storage. Therefore, thermogravimetric/differential thermal analysis and X-ray diffraction evaluations were conducted to determine the plutonium's crystal structure, oxide content, and moisture content; these analyses reported that the plutonium was predominately amorphous and tetrafluoride, with an oxide content near 10%. Freshly fluorinated plutonium tetrafluoride is known to be monoclinic. During the initial thermogravimetric/differential thermal analyses, it was discovered that an exothermic event occurred within the material near 414°C. X-ray diffraction analyses were conducted on the annealed tetrafluoride. The X-ray diffraction analyses indicated that some degree of recrystallization occurred in conjunction with the 414°C event. The following commentary describes the series of

thermogravimetric/differential thermal and X-ray diffraction analyses that were conducted as part of this investigation at PNNL.

2.2 Introduction

Radiolysis within plutonium oxide, plutonium metal, and halide salts resident within plutonium stores is well documented (*1*), (*2*), (*3*), (*4*), (*5*). In fact, radiolytic actions within plutonium matrices is one of the more investigated phenomena of radiolysis in the actinides series due to an overall, but certainly not a total, global shift from plutonium production to plutonium sustainability. This extends into the long-term storage of plutonium, whether for future uses or long-term disposal. Tandon conducted a detailed review on the effects of radiolysis in plutonium dioxide and its impurities as related to long-term storage containers (*6*). Tandon focuses on gas generation and degradation within plutonium salt matrices as a result of radiolysis (*6*). Through this focus, it was shown that there is significant evidence to support the hypothesis that alpha radiation, along with the subsequent recoil nucleus, is one of the more important drivers of radiolysis within plutonium matrices (*6*). This is illustrated with a description of localized effects due to the high linear energy transfer (LET) associated with alpha radiation, as compared with gamma or beta radiation (*6*). Furthermore, chemical changes are inherent within a material that is subjected to significant LET (*6*); of course, the extent and severity of the chemical changes are dependent on the frequency and intensity of the radiation in question (*6*). That being said, chemical changes within a plutonium bearing substance can be significant, resulting in localized crystal lattice expansion or melting within the substance. These chemical changes are characteristic within weapons grade plutonium because every atom will be displaced within a 10-year period due to the high flux of alpha radiation associated with it. The radiolysis is associated with the Frenkel and Schottky type defects as described by Johnson (*6*) (*7*). Frenkel and Schottky defects are the cation and anion vacancies that form from the ejection of crystal lattice ions. Frekel defects consist of interstitial cation and cation-vacancy pairs. Schottky defects consist of a pair of anion and cation vacancies within a crystal lattice (*7*). In the mechanisms of radiolysis, these crystal lattice defects are the result of radiation interactions within the lattice, radiation that imparts a sufficient amount of energy to overcome the molecular bond between the ions within the lattice. The ejected ions within plutonium, typically cations due to their smaller size and activity, can undergo diffusion and become trapped in interstitial sites of the crystal lattice (*6*).

Frenkel defects fit the characteristics of radiolytically damaged plutonium matrices well (*6*). This can be attributed to the small ionic radius of the plutonium cation and the lack of density loss with radiolysis in plutonium stores. With a high fluence substance like that of weapons grade plutonium, the combination of cation displacements from the direct actions of nuclear decay and anion displacements from decay interactions can lead to an amorphization of the plutonium lattice structures (*6*), (*8*). In fact, for every plutonium atom that decays, it has been estimated that 2,200 Frenkel pairs are created in the matrix (*5*).

This amorphization matches the condition as observed in the Hanford plutonium tetrafluoride and appears to follow a similar trend as found in the metamictization of uranium and thorium containing minerals. Alpha radiation and the recoil nuclei associated with it are typically responsible for the metamictization of actinides, but

Woodhead et al. identifies that the spontaneous fissions within uranium could be a driver as well (*9*). This is certainly an interesting perspective since the prevalence of alpha-n reactions in plutonium tetrafluoride are significant. This phenomenon can also be seen with the metamict transition of zircon when associated with actinide bearing minerals and provides what appears to be a parallel to the radiolytic degradation seen in plutonium matrices (*9*).

A macroscopic characteristic of these radiolytically driven microscopic diffusions/vacancies within a crystal lattice is color change. This color change is a byproduct of F center and V center formations within the lattice (*6*). F centers occur when an unbound electron fills an anion vacancy, and V centers occur when an anion loses an electron, converting it to a neutral atom, balancing a cation vacancy (*6*). At least in sodium chloride, the amount of radiolysis, and subsequently the F and V centers created, are responsible for color changes in the salt from “blue-black to light blue to purple to grayish-white”, as described by Tandon (*6*). This color change phenomenon explains why some crystal structure defects are referred to as color centers. Whether the lattice defect is an interstitial impurity, F center, V center, or other mechanism that results in electron and/or molecular changes within the crystal, there is a change in the amount and type of photons that interact with the materials’ crystals. This changes the specific wavelengths of light that are absorbed or reflected by and/or transmitted through the substance thereby changing the observed color of the substance.

Further phenomena are the effects that annealing has on the reversal of radiolysis, and if present, the color changes within a substance. Tandon found in his study that:

> Some variables also affect the initial rate of defect production by altering the fraction of electron-hole pairs that recombine at impurity sites and lose

> recombination energy with no defect production. Annealing of salt takes place by heating or exposing it to light and will lead to bleaching of the colors. By heating the irradiated salt to a few hundred degrees centigrade, the radiation-induced F and V1 centers can be removed. Electrons being released from the F centers combine with the electron-deficient V1 centers (*6*).

The focus of this work is to shed light into the reversibility of these radiolytically induced defects by recombination through annealing, and how temperature and time play a role in this reversal within Hanford produced plutonium tetrafluoride. The following sections will illustrate the initial documentation of these phenomena and confirmation of the phenomena through further analysis. This effort relies on the comparison of results from multiple thermogravimetric/ differential thermal and X-ray diffraction analyses.

2.3 Background

As part of a 2-year Laboratory Directed Research and Development (LDRD) Project at the Pacific Northwest National Laboratory (PNNL) to investigate the production processes that occurred at the Hanford Site in Washington State, U.S.A., a 50-year-old sample of plutonium tetrafluoride was used in re-establishing the metallothermic reduction of plutonium. Thermogravimetric/differential thermal and X-ray diffraction analyses were conducted as part of the LDRD project to understand the material's condition because of its unusual color and age. These analyses showed that the plutonium was predominately amorphous and tetrafluoride. However, freshly fluorinated plutonium tetrafluoride is known to be crystalline in its arrangement, and its structure is monoclinic (*10*).

The monoclinic structure of fluorinated plutonium tetrafluoride gives a repeating molecular unit consisting of opposing distorted pyramids that consist of a plutonium atom apex and a base of four fluoride ions (*10*). Each plutonium atom shares bonds with the four fluoride ions opposing it. The amorphous structure of the 50-year-old Hanford plutonium appears more akin to a glass structure, with little repetition in its structure. This combined with its unusual color suggested that oxidative, hydrolytic, or radiolytic damage had occurred throughout the material. The issue with simply oxidative or hydrolytic damage was that both species, PuH_x and PuO_x, are crystalline upon formation, not amorphous, plus, the tetrafluoride was stored in a sealed container.

A thermogravimetric/differential thermal analysis was conducted to determine if molecularly bound waters of hydration and/or hydrolysis were responsible for the unusual color of the plutonium tetrafluoride. Through the thermogravimetric/differential thermal analysis, it was discovered that heating the plutonium tetrafluoride in a stream of argon to approximately 414º Celsius resulted in an exothermic reaction that restored the plutonium tetrafluoride to its characteristic salmon pink color, returned a measurable portion of its crystal structure, and registered no appreciable mass loss (0.5% or less).

Much like when white sodium chloride is irradiated and a brown salt is produced, plutonium tetrafluoride appears to transition from a salmon pink to brownish-grey salt under adequate irradiation conditions. The irradiated/radiolytically damaged state of the plutonium tetrafluoride is not its ground state, rather an excited state of the system, consisting of locally induced defects like those of F center and V centers. As with all molecular systems, the plutonium tetrafluoride will drive towards a ground state of higher entropy, given that a sufficient amount of energy is imparted to it globally. Because external heat imparts global energy into a crystal structure, external heat can provide the energy needed to increase the vibrational modes of F center electrons and/or interstitial cations within the entire substance, more or less equally. This can drive electrons and ions within the crystal lattice to their ground state that is, in the case of plutonium tetrafluoride, a monoclinic arrangement. The result is a realignment of its defects, thereby reproducing its characteristic crystalline color. The exact form that these defects follow and to what extent their realignment is dependent on annealing time and/or temperature remains to be determined.

2.4 Study of the annealing effects on recrystallization of plutonium tetrafluoride

Thermogravimetric/differential thermal analyses were conducted in 2015 as part of a broad material characterization to determine the initial state of the Hanford plutonium tetrafluoride. The 2015 analyses demonstrated that the plutonium was in a previously unreported condition. Therefore, in 2016, further analyses were conducted to confirm and explore the nature of the 2015 results. The 2015 and 2016 analyses are the focus of this effort. The analyses were conducted in the Radiochemical Processing Laboratory (RPL) at the PNNL using a Seiko Instruments Incorporated, Exstar Thermogravimetric/Differential Thermal Analyzer 6200. The following is a detailed analysis of the obtained results.

2.4.1 Thermogravimetric/differential thermal analyses

The 2015 study began with a baseline thermogravimetric/differential thermal analysis that consisted of two empty alumina crucibles, one crucible on the reference probe of the instrument and one crucible on the sample probe of the instrument. The baseline curve is shown in Figure 2.1. The baseline analysis began at 25°C and terminated at 1050°C. Over the 1025°C temperature range, the differential thermal signal varied by approximately 51.0 μV, and the thermogravimetric signal varied by approximately 75.0 μg. This equates to a 0.074% deviation in mass of the empty sample crucible.

A calibration verification was performed on the Seiko Instruments Incorporated, Exstar Thermogravimetric/Differential Thermal Analyzer 6200. Indium, zinc, and silver metals were melted in the analyzer, and the known melting point of each metal was checked against the endothermic reaction captured by the Exstar's software. The results of the indium, zinc, and silver melt point verifications were within 0.47%, 0.47%, and 0.59% of the literature values, respectively (*11*), (*12*), (*13*).

Figure 2.2 illustrates the differential thermal analysis results for the first sample examined, a 38.4mg sample of plutonium tetrafluoride. Over the first 200°C, there was an initial mass loss of 0.38%. The mass remained constant from 200°C to 715°C but began to drop significantly as the temperature increased. Four energy variation events were observed on the differential thermal curve in Figure 2.2. There is a prominent exothermic peak at approximately 414°C and a prominent endothermic peak at approximately 875°C. There is a lesser exothermic peak at approximately 607°C and a lesser endothermic peak at approximately 1018°C.

The 414°C peak is consistent with an exothermic reaction due to recrystallization per the subsequent X-ray diffraction analysis and the lack of a significant loss in mass. This absence of mass loss during the 414°C exothermic event shows a correlation to the reversal of Frenkel defects, because as previously discussed, Frenkel defects are not accompanied by a change in density (*7*).

The 875°C endothermic peak is consistent with decomposition of plutonium tetrafluoride, as can be seen with the onset of a substantial mass loss reported by the thermogravimetric curve. The onset occurred above the stability limit as reported for plutonium tetrafluoride in air (600°C) (*10*) but below the reported melting point of plutonium tetrafluoride (1037°C) (*14*). The tetrafluoride will decompose to an oxide provided certain conditions are met. One would expect this transition to display a change in mass. Therefore, it can be theorized that the 875°C reaction is a combination of oxidation and decomposition.

The second sample of plutonium tetrafluoride analyzed contained twice the mass at 76.0 mg of the initial sample. Due to the apparent decomposition of the plutonium tetrafluoride and the lack of further recrystallization effects above 800°C, the second sample was limited to 700°C in the Thermogravimetric/Differential Thermal Analyzer. After the first heat cycle to 700°C, the sample was allowed to cool under argon and a second identical cycle was performed. This data is shown in Figures 2.3 and 2.4. The exothermic peaks observed in Figure 2.2 were repeated in cycle one but were not present in cycle two. Additionally, the second cycle had a mass gain of 0.21%, as opposed to the 0.51% mass loss seen with the first cycle. This illustrates that the exothermic event produced in cycle one at 414°C, and not repeated in cycle two, is a singular transition event. In other words, it is some form of instantaneous phenomenon, like that of recrystallization and/or defect realignment.

Figure 2.3 contains a close up of the 607°C exothermic event. There is some correlation between the two cycles at the 607°C exothermic event. This could suggest that the annealing effects in plutonium tetrafluoride increase with increased temperature or with increased time. The lack of sharpness in the 607°C exothermic reaction curve for the second cycle could indicate that once the initial instantaneous exothermic event occurs, further annealing can be accomplished but at a less intense rate.

Figure 2.5 illustrates the blackened condition of the plutonium tetrafluoride post the 875°C endothermic event. A comparison of two more thermogravimetric/differential thermal analyses is shown in Figure 2.6, a 24.5mg plutonium tetrafluoride sample and a 43.9mg plutonium tetrafluoride sample. The results are consistent across all of the single cycle analyses.

2.4.2 X-ray diffraction analyses

In order to determine the recrystallization affects from the 414°C and 607°C exothermic events, X-ray diffraction analyses were conducted on the 50-year-old Hanford plutonium tetrafluoride. Two separate approaches were taken with the X-ray diffraction analyses. A sealed plastic dome was used to hold an approximately 0.4g powder sample for the first analysis, and a glass microscopy slide with Kapton was used to contain a mixture of Krylon and approximately 0.2g of plutonium tetrafluoride for the second analysis. The dome is shown in Figure 2.7.

The diffractograms of two plutonium tetrafluoride samples are shown in Figure 2.8, one non-annealed sample and one annealed to 500°C. According to the analysis, the pattern for cubic plutonium dioxide is shown as small sharp peaks at roughly 28.6, 33.1, 47.5, 56.3, 59.1, 69.5, 76.8, 79.1, and 88.4 degrees, 2-theta, rising above the broad diffractogram of the plutonium tetrafluoride. However, the peak positions are displaced to lower 2-theta (higher d-spacings) compared with those expected for stoichiometric plutonium dioxide. At the same time, the multiplets of peaks expected for plutonium tetrafluoride, five at 21.3 to 27.2 and six at 43.3 and 50.0 degrees, two-theta, are not present except as broad mounds or contributors to the background.

The lack of plutonium tetrafluoride X-ray diffraction peaks in the untreated sample is most likely due to its metamictization. The lower 2-theta (higher d-spacing) of the plutonium oxide could be a consequence of a crystal lattice expansion due to radioactive decay (*15*). This phenomenon is well studied (*15*). The radiolytic lattice expansion is opposed by thermal relaxation back to the original atomic spacing (*6*). However, at room temperature, the radiolytic processes in plutonium oxide occur with enough frequency that an equilibrium lattice expansion is reached (*6*). It is also observed that no X-ray diffraction line broadening is witnessed and thus no static defect clusters form in the lattice (*15*). The plutonium oxide peaks observed in the diffraction patterns are sharp, as shown in Figure 2.8.

For nominal 94% Pu-239 and 6% Pu-240, the projected rate of lattice expansion is given in Figure 2.9 (*15*). It is seen that the lattice expansion plateaus at 5.4164 Å, after an initial value for fresh stoichiometric plutonium oxide of 5.3982 Å. The terminal value is near the lattice constant of 5.4188 Å observed for the plutonium oxide in the legacy plutonium tetrafluoride. The calculation also shows that lattice expansion is essentially complete in ≈10 years at room temperature, meaning that the plutonium oxide in the legacy plutonium tetrafluoride, dating from 1966, had ample time to reach its plateau value at room temperature. This time scale for lattice expansion terminus in plutonium oxide agrees with the estimation by Tandon, as well (*6*).

Further X-ray diffraction analyses were chosen based on the color restoration seen with the two 500°C and 650°C annealed samples. Figure 2.10 illustrates the increased crystallinity of the plutonium tetrafluoride annealed to 650°C.

The 650°C sample had contained a greater mass than the 500°C sample, approximately 35.0 mg as opposed to approximately 25.0 mg. Therefore, it is difficult to draw certain conclusions on the differences between the two samples. The model was in better agreement with the 650°C data than with that of the 500°C data. The weight percent from Rietveld refinement reported that both samples contained approximately 94 percent plutonium tetrafluoride and 6 percent plutonium oxide, but this does not account for any amorphous components that are clearly still present in both samples. A series of test are currently underway to quantify the amount of amorphous plutonium tetrafluoride present with various annealing temperatures.

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2.5 Conclusion

The plutonium tetrafluoride that was separated over 50 years ago at the Hanford Site was analyzed because of its age and unusual color. There were questions about the condition of the material that had to be answered in order to determine the suitability of the material for future use or long-term storage. The subsequent thermogravimetric/differential thermal and X-ray diffraction evaluations illustrated that the plutonium's crystal structure had transitioned from monoclinic (freshly fluorinated) to amorphous; its oxide content was near 10 percent; and its moisture content was shown to be less than 1 percent according to the lack of mass loss at dehydration temperatures;

During the initial thermogravimetric/differential thermal analyses, it was discovered that an exothermic event occurred within the material near 414°C. X-ray diffraction analyses were conducted on the annealed tetrafluoride and indicated that some degree of recrystallization occurred in conjunction with the 414°C event. The thermogravimetric/differential thermal analyses also illustrated that a second, lesser exothermic event occurred within the material near 607°C. X-ray diffraction analyses indicated that a greater degree of recrystallization occurred in conjunction with the 607°C event. A greater degree of freshly fluorinated color was restored in the plutonium tetrafluoride at the 607°C event as well. Whether this higher state of recrystallization at the 607°C event was the result of greater temperatures or greater annealing time remains to be seen in continuations of this work.

Although further investigations into the annealing phenomena of plutonium tetrafluoride remain for a continuation, clearly, the radiolytic metamictization of plutonium tetrafluoride is in contradiction to that of plutonium dioxide. However, plutonium tetrafluoride may subscribe to the same damage plateau timeline of approximately 10 years, with alpha radiation from the plutonium being a primary driver of its damage.

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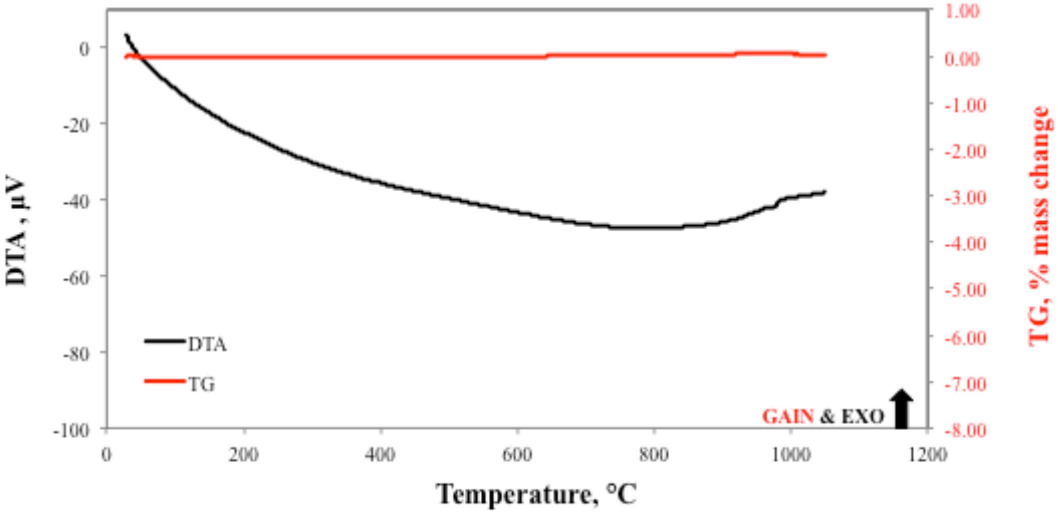

Figure 2.1 2015 thermogravimetric/differential thermal baseline analysis. This illustrates the mass (right y axis) and energy (left y axis) variations from the empty alumina crucibles with increased temperature (x axis) in argon gas. This thermogravimetric curve is subtracted from the analyses provided in Figures 2.1-2.7 to remove any variations that are a result of phenomena associated with the crucibles. The differential thermal curve illustrates that there are no instantaneous exothermic or endothermic events associated with the empty crucibles, only gradual changes with increased temperature as expected. A second baseline analysis was conducted in 2016.

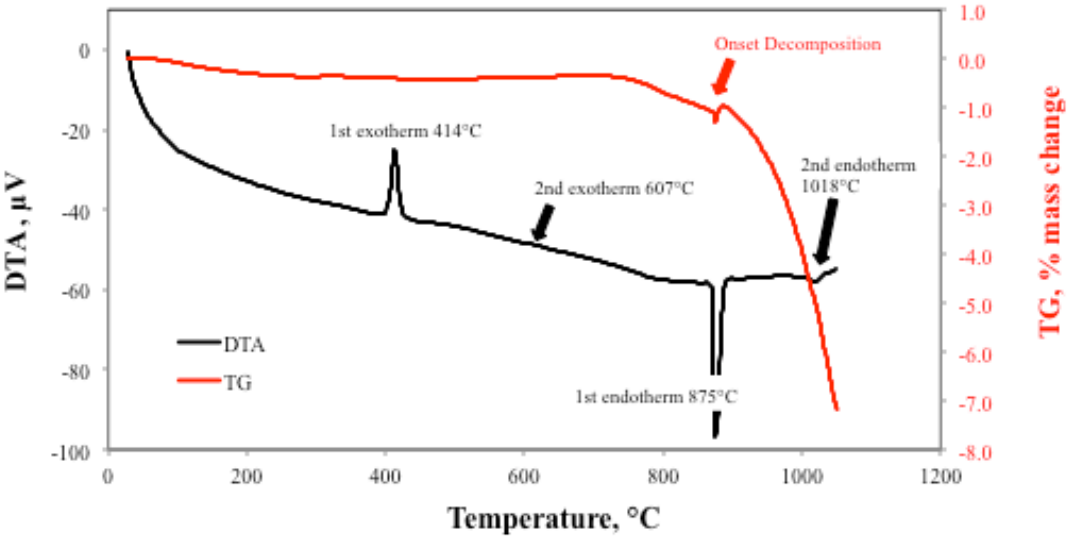

Figure 2.2 Initial thermogravimetric/differential thermal analysis with 38.4mg plutonium tetrafluoride. This illustrates the mass (right y axis) and energy (left y axis) changes of a 38.4mg sample of plutonium tetrafluoride with increased temperature (x axis) in argon gas. The thermogravimetric baseline from Figure 2.1 is subtracted from these curves to minimize any contribution from the alumina crucible. An exothermic reaction (release of energy) can be seen on the differential thermal (black line) curve at 414°C and to a lesser extent 607°C. An endothermic reaction (absorption of energy) can be seen on the same curve at 875°C that corresponds to the onset of a mass loss on the thermogravimetric (red line) curve. There is a lesser endothermic peak at 1018°C that remains unexplained.

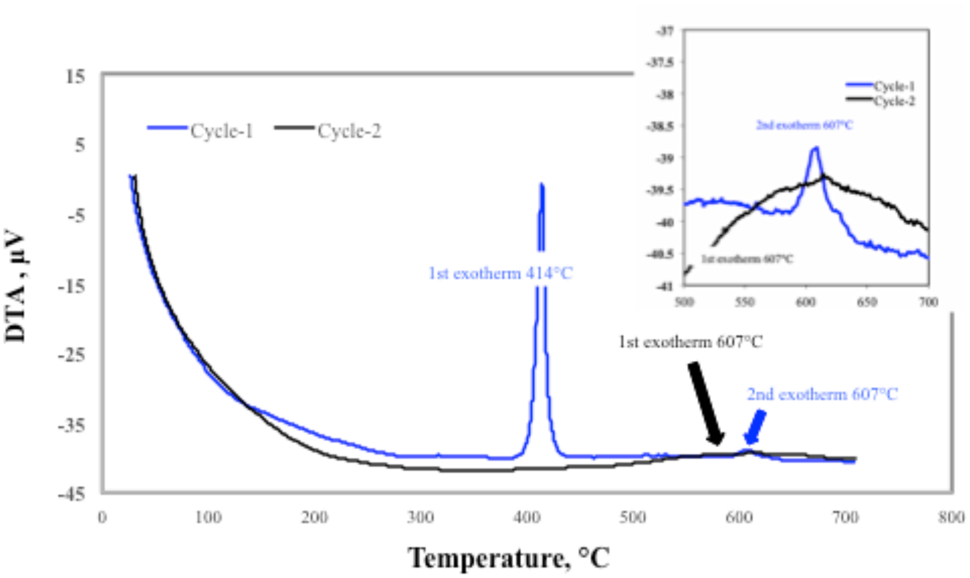

Figure 2.3 2015 Cycled differential thermal analysis with 76.0mg plutonium tetrafluoride. This illustrates the energy (y axis) released by a 76.0mg sample of plutonium tetrafluoride with increased temperature (x axis), in argon gas. The thermogravimetric baseline from Figure 2.1 is subtracted from this analysis. The sample was analyzed twice without removing it from the analyzer. An exothermic reaction (release of energy) is shown on the differential thermal curve of the first cycle (blue line) at 414°C and 607°C. An exothermic reaction is also evident on the differential thermal curve of the second cycle (black curve) at 607°C only and with less instantaneousness than that of the first cycle.

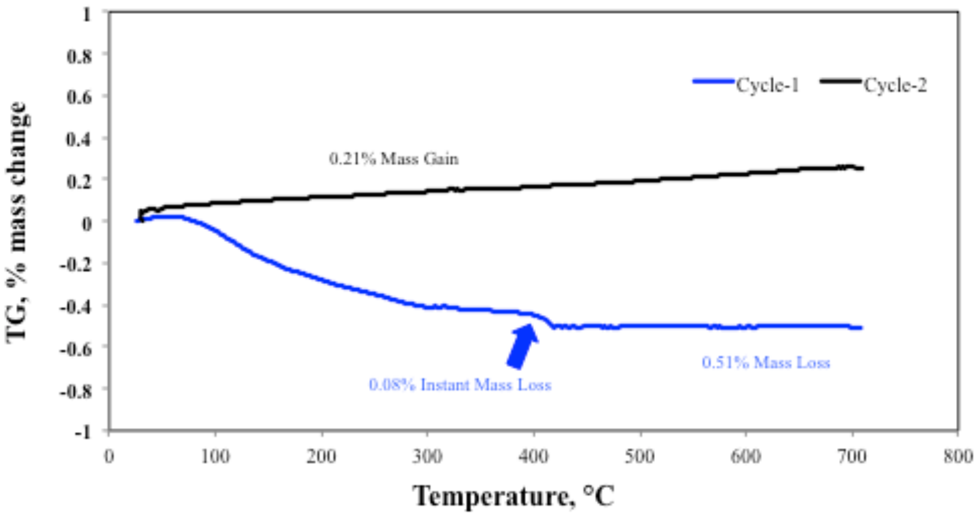

Figure 2.4 2015 Cycled thermogravimetric analysis with 76.0mg of plutonium tetrafluoride. This illustrates the mass (y axis) change of a 76.0mg sample of plutonium tetrafluoride with temperature change (x axis) in argon gas. The thermogravimetric baseline from Figure 2.1 is subtracted from this analysis. The sample was analyzed twice without removing it from the analyzer. A gradual mass loss to approximately 0.51 percent can be seen on the thermogravimetric curve of the first cycle (black line) up to the 414°C event, with an instantaneous loss of 0.08 percent. In contrast, a gradual mass gain of 0.21 percent can be seen on the thermogravimetric curve of the second cycle (blue line) over the entire temperature range (20-700°C). Although these mass differences are not significant, their opposition is interesting.

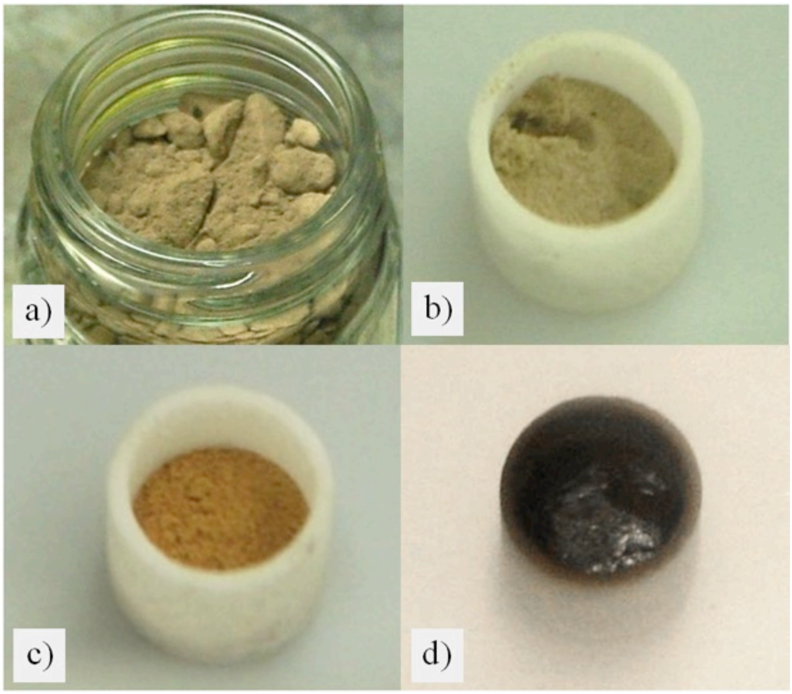

Figure 2.5 Plutonium tetrafluoride samples a) aged State, b) 350°C, b) 450°C, and c) 1050°C. This illustrates the various states of color change within the material. There is clearly only a slight color change, if any, between its aged state and 350°C annealed state. The plutonium annealed to 450°C shows a significant color change, and the 1050°C annealed material demonstrates a post-melt color.

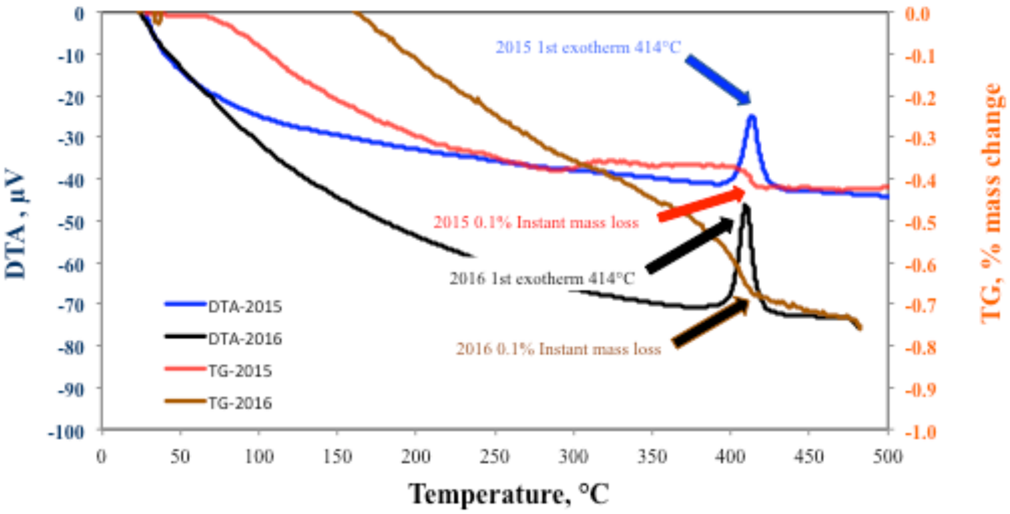

Figure 2.6 Thermogravimetric/differential thermal analysis comparison of plutonium tetrafluoride from 2015, 24.5mg, and 2016, 43.9mg. This graph illustrates the mass (right y axis) and energy (left y axis) changes from these two samples of plutonium tetrafluoride with temperature change (x axis) in argon gas. The thermogravimetric baseline from Figure 2.1 is subtracted from the 2015 analysis. A thermogravimetric baseline for the 2016 is subtracted from the 2016 analysis. The exothermic reactions (release of energy) are shown for the 2015 (blue line) and 2016 (black line) differential thermal curves at 414°C and illustrate repeatability of the reaction. The 607°C exothermic event was not compared, as the onset of crystallization was the focus. The thermogravimetric curves for the 2015 (red line) and 2016 (brown line) analyses show good agreement with a steady mass loss up to the 414°C event, at which an instantaneous mass loss (approximately 0.1%) occurs in both samples.

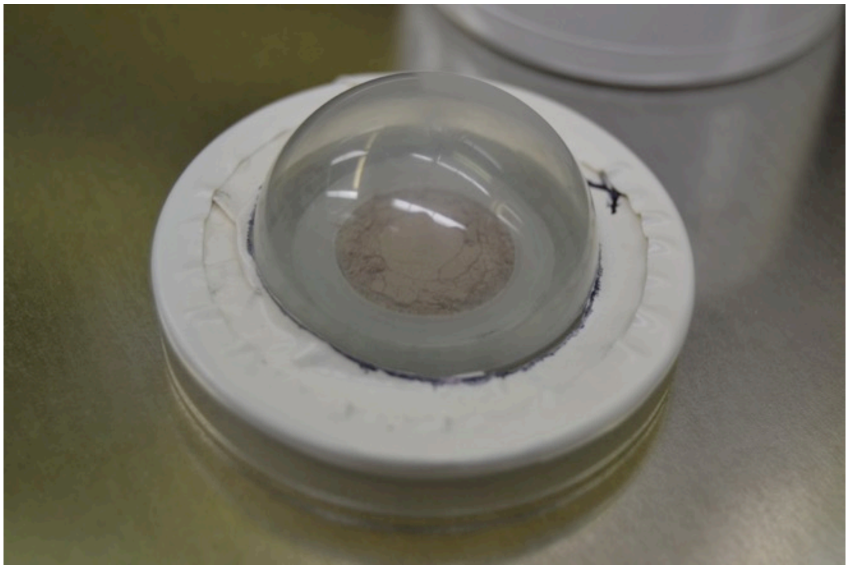

Figure 2.7 Approximately 0.4g of aged (non-annealed) plutonium tetrafluoride in X-ray diffraction dome.

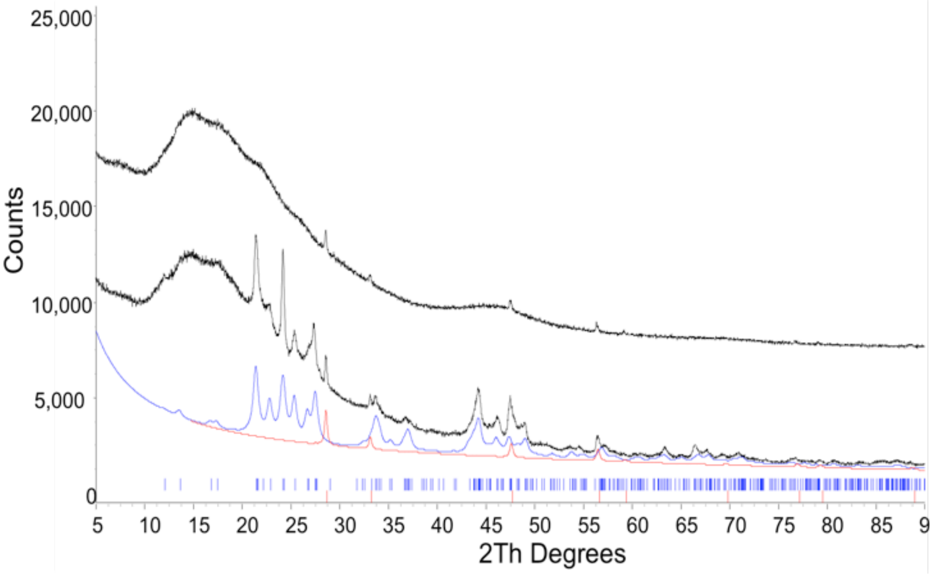

Figure 2.8 Diffractogram of aged (non-annealed) plutonium tetrafluoride (black, top), 500°C annealed plutonium tetrafluoride (black, middle), plutonium oxide modeled pattern (red), and plutonium tetrafluoride modeled pattern (blue) [patterns are shifted vertically for clarity].

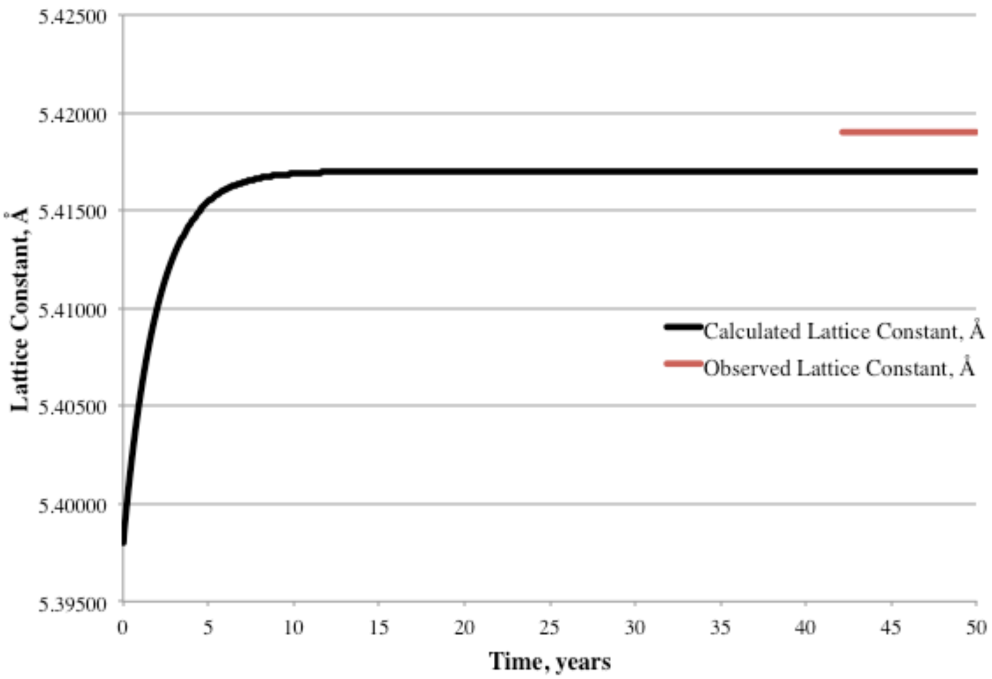

Figure 2.9 Comparison of calculated and observed PuO_2 lattice constant increase, Å, (y axis) with time (x axis) in years for plutonium oxide (*15*). This graph clearly illustrates that plutonium oxide sustains a significant amount of radiolytic lattice expansion in 10 years or less, indicating that metamict transition in the Hanford plutonium tetrafluoride should follow the same trend.

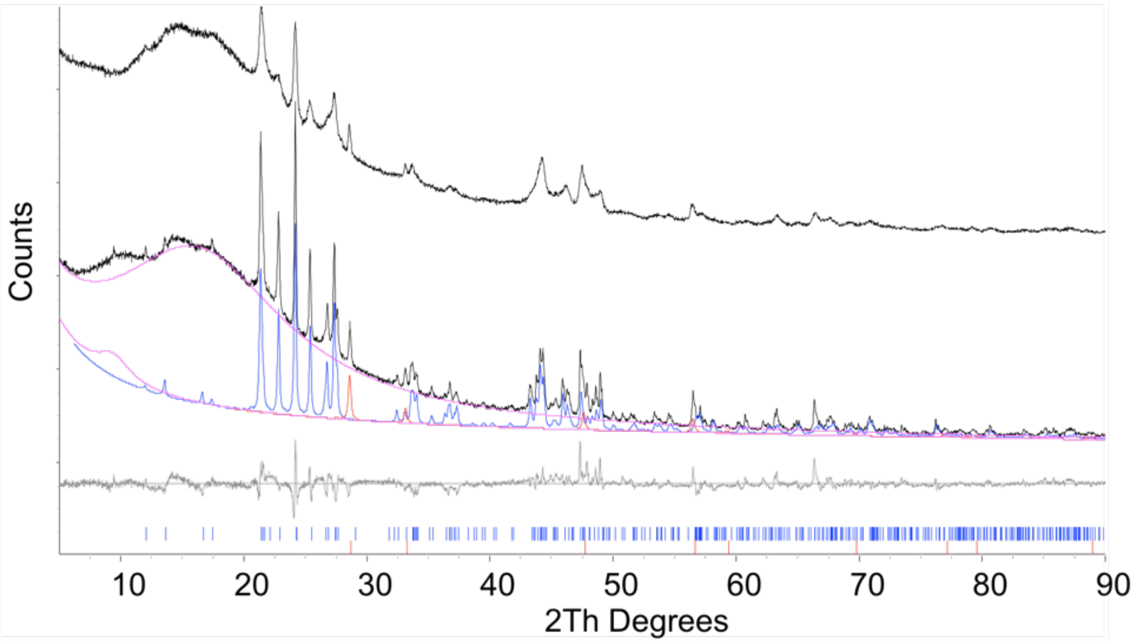

Figure 2.10 Diffractogram of 500°C annealed plutonium tetrafluoride (black, top), 650°C annealed plutonium tetrafluoride (black, middle), plutonium oxide modeled pattern (red), and plutonium tetrafluoride modeled pattern (blue) [patterns are shifted vertically for clarity]. Clearly, the sample annealed to 650°C (black, middle) shows good agreement with the modeled pattern (blue) of freshly fluorinated plutonium tetrafluoride. The question remains if this increased recrystallization at 650°C is attributed to the increased temperature or increased time of the annealing process.

CHAPTER 3

SHORT-TERM ANNEALING OF AMORPHOUS PLUTONIUM TETRAFLUORIDE

3.1 Abstract

An approximately 50-year-old sample of plutonium tetrafluoride has been analyzed at the Pacific Northwest National Laboratory (PNNL). The sample was produced at the Hanford Site's Plutonium Finishing Plant (PFP) and has been stored within sealed containers since the 1970s. Samples of this material have been used to study the amorphization of plutonium tetrafluoride due to self-induced alpha-radiolysis under long-term storage conditions, and the reordering of its original crystal lattice structure under annealing conditions. This work investigates the effect that various short-term annealing temperatures have on the percentage of that reordering and the ingrowth plutonium oxide.

3.2 Introduction

An approximately 50-year-old sample of plutonium tetrafluoride that was produced at the Hanford Site has been analyzed at the Pacific Northwest National Laboratory (PNNL) since 2014 (*1*). This sample represents one of the last remaining stocks of plutonium tetrafluoride that was produced at the Plutonium Finishing Plant (PFP). The sample has provided invaluable insight into the condition of bulk plutonium tetrafluoride under long-term storage conditions, instead of the metal and oxide forms as typically seen and as stipulated by the Department of Energy's DOE-STD-3013-2012 (*2*).

Freshly fluorinated plutonium tetrafluoride is monoclinic and displays a salmon pink color (*3*). However, as with other plutonium compounds, if given enough time, it can undergo amorphization through radiolysis (*4*). Once crystalline plutonium has undergone amorphization, the compound can be annealed to restore at least some degree of its crystalline structure (*1*), (*4*), (*5*). The work presented here is based on this cycle of radiolysis and crystal structure reordering in plutonium tetrafluoride through brief annealing periods at temperatures between 350°C and 650°C.

3.3 Background

3.3.1 Comparison to plutonium dioxide

There have been a number of studies on the radiolytic expansion of the crystal lattice spacing in plutonium and uranium oxides, and the effect that annealing has on the reversal of the radiolytic damage (*4*), (*5*), (*6*). Turcotte and Chikalla explored the phenomena with regards to the 238 isotope of plutonium oxide in depth (*5*). Weber looked at the phenomena in cerium oxide, uranium oxide, and plutonium oxide where the alpha radiation from two plutonium isotope 238 sources was used (a high activity external alpha source greatly reduces the effect of alpha-recoil progeny nucleus of internal alpha decay) (*6*). Although the study presented here is focused on the radiolysis and annealing effects in plutonium tetrafluoride and was not based on Turcotte and Chikalla's or Weber's works, there are similarities and differences worth addressing. Clearly, plutonium oxide and plutonium fluoride do not share the same crystal structure.

Plutonium dioxide displays a face-centered cubic structure (*3*), and plutonium tetrafluoride displays a monoclinic cubic structure (*3*). However, the mechanisms of alpha-induced radiolysis have been shown to follow a similar trend in many different compounds (*4*), (*7*), (*8*). An earlier work by McCoy et al. noted some of these mechanisms (*1*).

Interestingly, the significance of alpha radiolysis as a prominent factor responsible for lattice defects in actinide oxides is also seen with the Nakae et al. work on fission-induced crystal lattice parameter expansions in uranium oxides (*9*). Nakae et al. demonstrated that in uranium oxides with a grain size of 2.5 μm and irradiated at a dose of $10^{14} – 10^{15}$ fissions/cm^3, an initial decrease in the uranium's crystal lattice parameter is probable (*9*). This decrease has not been reported with regards to alpha radiation-induced lattice parameter changes in plutonium or uranium oxides, at any dose level (*6*), nor has it been reported with the self-induced alpha radiolytic lattice parameter changes in plutonium tetrafluoride (*1*). There is the appearance of a crystallite size decrease in tetrafluoride due to the loss of order once amorphization is predominant. Whether this amorphization is due to a lattice parameter decrease, a defect saturation point, or other mechanism, has yet to be determined.

The metamictization in plutonium tetrafluoride appears to follow the same crystal lattice defect formation as alpha-radiolytic lattice parameter expansion that is present in plutonium oxides (*1*). This follows logic, because there is significant evidence that a portion of the crystal lattice expansion that occurs in plutonium oxides is due to self-induced alpha radiolysis (*4*), (*5*), (*6*). The age of, and subsequently the cumulative radiation dose to, the oxide has a great bearing on the value of that lattice parameter expansion (*4*), (*5*), (*6*). In plutonium tetrafluoride, the age of, and subsequently the cumulative radiation dose to, the material appears to have a great bearing on the value of its amorphization and color change.

Weber demonstrated a lattice parameter expansion comparison of externally alpha irradiated plutonium oxide (plutonium 239 irradiated on both sides with plutonium 238 sources) with that of self-induced alpha irradiated plutonium oxide (plutonium 238 only, no external source) (*6*). The crystal lattice expansion was greater in samples exposed to an external alpha radiation source than that of the self-irradiated samples at dose equivalents (*6*). Weber further noted that single crystal samples suffered a greater lattice parameter expansion as a result of external alpha radiation than that of polycrystalline samples (*6*). This is seen as relatable to the previously noted Nakae et al. work with particle size influence on fission-induced damage in uranium oxides (*6*) and could be the baseline for a single crystal radiolysis experiment with plutonium tetrafluoride.

3.3.2 Mechanisms of defect formation

The crystal lattice parameter expansion due to alpha-radiolysis in bulk actinide oxides is mainly a consequence of Frenkel defects and helium interstitials. The defects in plutonium decay are formed primarily by 5-mega electron-volt (MeV) alpha particles and 87-kilo electron-volt (keV) recoil nuclei of the uranium 235 progeny isotope (*6*). Frenkel defects are cations and/or anions that have been removed from ideal crystal lattice positions and are trapped within interstitial sites. Linear energy transfer (LET) from an alpha particle and its recoil nucleus to crystal lattice ions is the driver of Frenkel defect formation. Alpha particles emitted from plutonium atoms are estimated to penetrate approximately 10-11.5 μm into a compound, with the subsequent uranium recoil nucleus penetration lesser at near 20 nm (*6*), (*10*).

Alpha particles transfer most of their energy through the ionization of crystal anions and cations (*10*). This results in the production of free electrons that combine with alpha particles for the formation of helium atoms and either cations with higher ionization states or neutral atoms from anions (*11*). These ionization changes also result in an increase to the charge vacancies within the crystal (*11*).

There are different reports on the number of defects produced by alpha particles and recoil nuclei in plutonium. Weber has predicted that near the end of their track, alpha particles produce up to 1500 dislocated ions in a plutonium oxide crystal through elastic collisions (*6*). Tandon and Wolfer report that alpha particles produce less than 500 defects in plutonium oxide and plutonium metal (*4*), (*8*). On the other hand, recoil nuclei transfer the majority of their energy through elastic collisions with local crystal ions (*10*). Weber et al. first estimated that a displacement cascade of hundreds of isolated ions were dislocated per recoil nucleus (*10*). However, in subsequent work, Weber has hypothesized that the defects created by the recoil nuclei could cluster at room temperature, as opposed to only clustering at elevated temperatures (*6*), (*12*). This is significant because a cluster of defects results in a lower value of crystal volume expansion per defect (*6*). In contrast to this, Tandon and Wolfer report that the recoil nuclei produce defects that number over 2000 and that clustering is inherent (*4*), (*8*). This could imply that the effect of defect clustering is responsible for the lower crystal volume expansion and therefore the lower estimation of isolated defect formation per decay by Weber (*6*), (*12*).

The 239 isotope of plutonium emits over 2.3 million alpha particles per milligram per second (*3*). Therefore, plutonium-239 has the potential to form more than 3 billion Frenkel defects per milligram per second, although a majority of these defects are reported to recombine within picoseconds of their formation (*7*). Furthermore, the plutonium cation is subject to a greater probability of displacement by the alpha particle or recoil nucleus due to its significantly smaller ionic radius (0.86 Å for Pu^{4+}) than that of the oxygen (1.38 Å) or fluorine (1.31 Å) anion (*3*).

3.4 Experimental approach

3.4.1 Short-term annealing of plutonium tetrafluoride

In order to investigate the rapidity of annealing mechanisms in plutonium tetrafluoride, 7-1.0g plutonium tetrafluoride samples were annealed within a MTI Model KSL-1100X muffle furnace at PNNL. The muffle furnace chamber was 1 liter in volume. The furnace is contained within a glovebox at PNNL's Radiochemical Processing Facility (RPL). The furnace was continuously purged with argon gas at a rate of approximately 5 liters per minute. For each anneal, approximately 1.0g of plutonium tetrafluoride was split into 0.5g samples to increase the surface area available for reaction. Each 0.5g sample was placed within an approximately 10.0 milliliter magnesium oxide crucible with a loose-fitted magnesium oxide lid. The crucible lids were loose-fitted to ensure that an adequate flow of argon reached the plutonium tetrafluoride within. Figure 3.1 illustrates the plutonium tetrafluoride within the magnesium oxide crucibles.

Five of the 1.0g sample sets were annealed at the approximate exothermic recrystallization event temperature of 414°C as reported in McCoy et al. (*1*). These annealing temperatures were set at 350°C, 380°C, 410°C, 430°C, and 460°C. Two of the sample sets were annealed in excess of the second exothermic event temperature of 607°C as reported in McCoy et al. (*1*). These annealing temperatures were set at 620°C and 650°C. The annealing curves are shown in Figure 3.2. The temperature data was collected from a calibrated Omega Type K thermocouple located within the furnace chamber and a J-KEM thermocouple reader/over-temperature controller that was connected to a laptop with J-KEM data logging software. The thermocouple reader and computer were located outside of the glovebox. As can be seen in Figure 3.2, the furnace controller overran the temperature setting for each anneal. This was not seen as detrimental to the analysis, as the instantaneousness of reaction at a given temperature range was the focus.

The samples were stored within glass vials under an air atmosphere until the X-ray diffraction specimens were prepared. Seven – 0.5g post-annealed samples are shown in Figure 3.3 and Figure 3.4 illustrating the comparison of 0.5g samples of plutonium tetrafluoride with Munsell color chart tabs.

3.5 X-ray diffraction analyses

Each set of annealed plutonium tetrafluoride was combined onto one Bruker A100B33 X-ray diffraction specimen holder. The plutonium was sealed onto the specimen holder with a layer of 3511 Kapton®. Silicon grease was placed within the snap ring well of the Bruker specimen holder to trap any plutonium particles not contained by the 3511 Kapton®. Figure 3.5 displays 1.0g of 350°C annealed plutonium tetrafluoride within the Bruker sample holder. As can be seen with Figure 3.5, 1.0g of plutonium compound was not adequate to fill the entire A100B33 well. Therefore, as is illustrated in Figure 3.6, a 0.755-inch inner diameter 1100 series aluminum washer was fit into each A100B33 well for the remaining six specimens. This reduced the A100B33's well volume by near 25 percent. The 350°C annealed sample was removed from the study due to its inadequacy in terms of crystal structure reordering and specimen preparation.

The samples were analyzed with a Rigaku Ultima IV powder X-ray diffractometer equipped with a Cu X-ray tube operating at 40 kilo-volts (kV) and 40 milliamps (mA), a vertical θ/ θ goniometer with a 285 millimeter radius, and a D/teX linear position sensitive silicon strip detector located within the RPL. A nickel filter was used to reduce the amount of diffracted k_β X-rays observed. An Eulerian cradle with automated sample height adjustment and sample rotation was also used. The instrument was configured to perform an automated sample alignment routine that adjusted the sample height to the proper position prior to data collection.

Full pattern Rietveld refinement was performed using the TOPAS v5 Bruker software package. Fundamental parameter type peak shapes were used in the refinement. The instrument contribution to peak broadening was determined by fitting three functions, a Lorentzian function with 1/cosine (θ) dependence, a hat function and a circles function with 1/tangent (θ) dependence, to a SRM 640d diffraction pattern standard supplied by the National Institute of Standards and Technology (NIST). The NIST standard and plutonium samples were analyzed with equal slit settings. The instrument zero error was also determined using the NIST SRM 640d. The crystallite size reported was determined using the Double-Voigt approach as implemented in the TOPAS v5 (Bruker) software package (*14*). The crystallite size reported was from the peak integral breadth of the Lorentzian type convolution to the peak shape. An assumption of spherical crystallites is made in this determination. A first order Chebychev polynomial with a 1/x function was used to model the background. An external standard method developed by O'Conner et al. (*15*) and Jansen et al (*16*) was used for quantification. The standard used for the external quantification method was a NIST SRM 676a. The NIST SRM 676a was analyzed within a Bruker specimen holder and Kapton® identical to that of the plutonium samples.

The Kapton® polyimide film that was used to contain each plutonium powder sample contributed to the diffraction pattern in the form of amorphous (broad) peaks at 14.933° and 18.8945° 2θ. These peaks along with additional broad peaks observed in the 380°C – 410°C annealed samples (around 23° and 47° 2θ) were modeled with freely refined peaks. An attempt was made to use the refined plutonium tetrafluoride structure, fitted to the broad peaks observed in the 380°C – 410°C annealed samples. This attempt did not result in a satisfactory fit. The addition of freely refined peaks allowed for the accurate calculation of known phase peak areas in the presence of unknown amorphous components. Since the same Kapton® film was used when collecting the 100% crystalline reference standard (SRM 676a), the film was not counted towards the sample amorphous content.

The structure of neptunium tetrafluoride as reported by Zachariasen was used as a starting point for the structure of plutonium tetrafluoride (*17*). The unit cell parameters were set to refine the pattern collected from the 620°C sample. The resulting unit cell parameters were a = 12.6074(7) Å, b = 10.6408(6) Å, c = 8.2447(5) Å, β = 126.328 (4)°. The resulting refined structure was fixed and used for the refinement pattern models of the remaining samples. Structures for plutonium dioxide and plutonium tetrafluoride hydrate were also used to model the observed diffraction patterns (*18*) (*19*). Figure 3.7 illustrates the diffraction patterns for the 6-1.0g samples (from 380°C-620°C), vertically shifted about the y-axis for comparison. The 350°C annealed sample was eliminated from the report due to the lack of crystal structure reordering and sample preparation.

3.6 Discussion

According to the trend illustrated in Figure 3.8, amorphous plutonium tetrafluoride appears to begin recrystallization on short time scales (< 1 hour) above 410°C in an inert atmosphere. This corresponds well with the 414°C exothermic event of recrystallization as suggested in McCoy et al. (*1*). There is also a clear trend that plutonium dioxide does not appear to form below 430°C in short-term annealing. There is clear evidence that the crystallite size of plutonium tetrafluoride increased as its defect concentration decreased. This was accompanied by a decrease in the crystallite size of plutonium oxide present in the sample. One of the most interesting phenomena can be seen in the close matching parabolic nature of the amorphous content and plutonium oxide crystallite size, while the crystallite size of plutonium fluoride continues in a more linear fashion.

The data also illustrates that plutonium tetrafluoride begins to calcine near 460°C under these conditions. It was expected that some degree of oxidation would occur at temperatures near 600°C. Therefore, it is not unreasonable to see a 2 percent by weight conversion at 460°C. The 500°C-600°C region was not studied in this work. But it would be worthwhile to investigate the oxide formation in this region under various argon flow rates. At this time, the data does imply that annealing temperatures above 430°C are not suggested if a measureable amount of oxide formation is undesirable. Longer annealing times (>12 hour) at near 400°C appear to be more suited for higher purity re-crystallizations.

The data further illustrates that approximately 2 percent of plutonium oxide and 2 percent plutonium tetrafluoride hydrate was present within the amorphous content as a crystalline phase prior to any reported anhydrous tetrafluoride recrystallization. This suggests that the plutonium oxide was either resident in the bulk material as a result of radiolytic mechanisms or that plutonium oxide is more resilient to the effects of radiolysis in the presence of plutonium fluoride, having remained crystalline over the approximately 50 years of storage. The latter theory seems contradictory to the previously discussed works on the amorphization of plutonium oxide (*4*), (*5*), (*6*). As far as the existence of the hydrated tetrafluoride, it appears that it could be present at the onset of crystal structure reordering. The tetrafluoride hydrate peak has not been seen in the analyses of the non-annealed specimens, although the non-annealed specimen holders have been of a different type (*1*). Plutonium tetrafluoride hydrate is orthorhombic and only shown in Table 3.1 as present at 2 percent by weight (*3*). Therefore, its existence as an intermediate phase between room temperature and 350°C is not intuitive based on the monoclinic phase of the anhydrate.

The existence of this crystalline oxide phase could have resulted through oxidative/hydrolytic reactions of the tetrafluoride with moist argon gas during sample anneal. Pre-purified bottled argon gas with an inline desiccator was used to purge the furnace chamber. Therefore, it is unlikely that this was responsible for the oxidation. If the hydrate was present in the bulk sample, just undetected until now, it is possible that 5 liters per minute of argon gas was insufficient to flush the hydration from the furnace chamber as liberated from the plutonium fluoride above 380°C. The removal of these hydrates corresponds somewhat to the ingrowth of plutonium dioxide. However, further tests need to be performed to determine the source of this oxidation, being that it does not match the literature (*3*), (*13*).

3.7 Conclusion

The work presented here is based on a cycle of radiolysis and crystal structure reordering in plutonium tetrafluoride through brief annealing at temperatures between 350°C and 650°C. The plutonium tetrafluoride studied was part of the last remaining stock of plutonium tetrafluoride made at the Hanford Site's PFP and has been in storage for near 50 years. It has clearly undergone radiolytically induced amorphization similar to that seen in plutonium dioxide stored for equal periods of time. However, the crystal lattice deformation mechanisms and those mechanisms that occur in plutonium tetrafluoride during the annealing process may not line up equally as well to those that occur in plutonium oxide.

There is a clear trend in this study of oxide formation in plutonium tetrafluoride that has been annealed at temperatures in excess of 430°C for short time periods of time (<0.5 hour above 400°C) in an argon atmosphere. This is significantly lower than the stability of plutonium tetrafluoride in an inert atmosphere as reported by Clark et al. (*3*). This result may be related to the stability of the tetrafluoride hydrate as reported by Cleveland (*13*), if the argon flow rate for this work was not great enough to remove the atmosphere before oxidation/hydrolysis of the plutonium took place. A study to investigate the lower threshold of this oxidation/hydrolytic reaction as a function of inert gas flow rate is warranted to quantify this assumption.

This work has posed some interesting questions about the stability of plutonium tetrafluoride in air and what mechanisms effect its recrystallization once amorphization has consumed the material.

3.8 Acknowledgement

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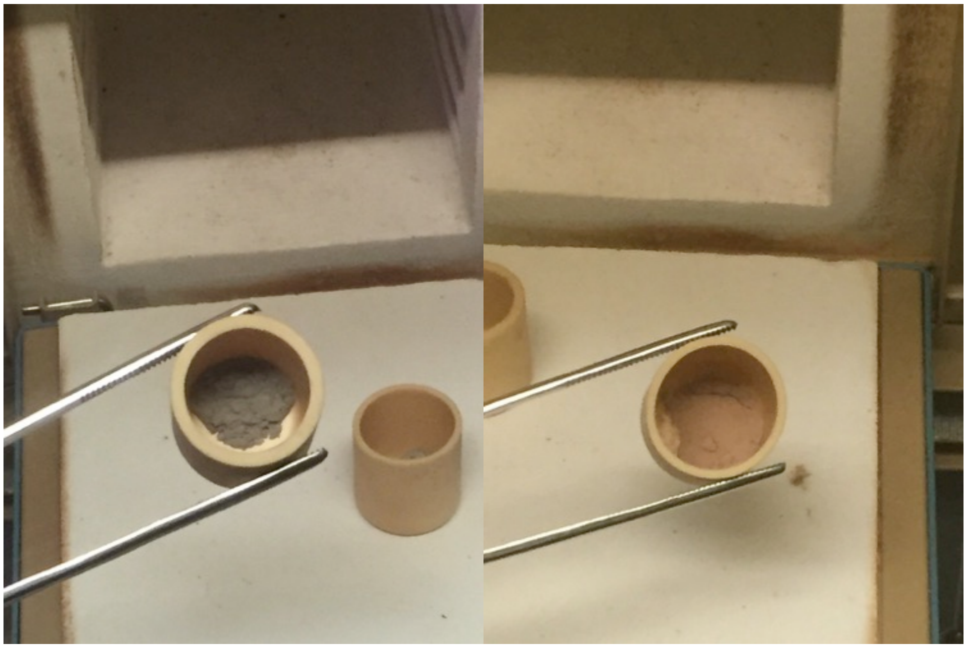

Figure 3.1 Plutonium tetrafluoride (PuF_4) within magnesium oxide crucibles; pre-annealing (left); post-annealing 620°C (right); the color change resident in the post-anneal sample is characteristic of defect elimination. The salmon pink color is typical for freshly fluorinated PuF_4. The greyish color is consistent throughout the approximately 50-year-old Hanford PuF_4 stock.

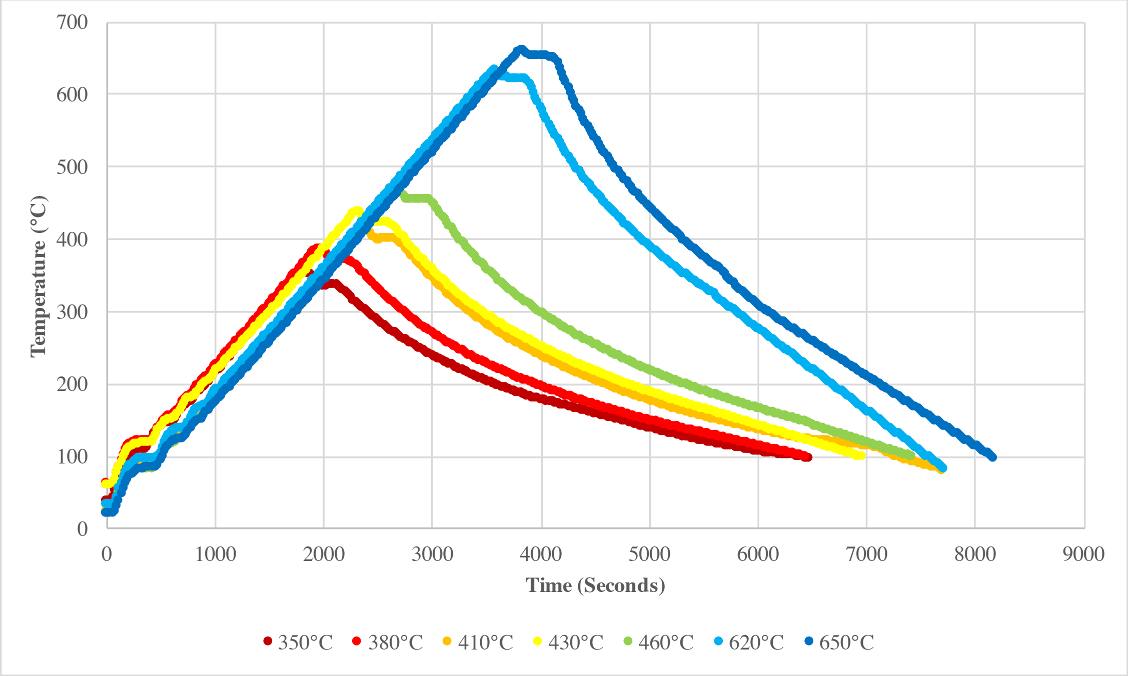

Figure 3.2 Annealing rate curves for 7-1.0g PuF_4 samples in MTI KSL-1000X muffle furnace purged with argon gas at 5 liters per minute. The furnace ramp rates were chosen to match the thermogravimetric/differential thermal analyzer ramp rates as reported in (*16*). The PuF_4 samples were left under an argon atmosphere until a temperature below 100° was reported by the J-KEM software. The hold time at temperature was an artifact of the furnace and not part of the program; this work was focused on the annealing effect of a maximum temperature and not necessarily soak time at temperature.

Figure 3.3 0.5g samples of PuF_4 annealed at (from left to right) 350°C, 380°C, 410°C, 430°C, 460°C, 620°C, and 650°C. There is a clear transition in the material from grey at a predominately amorphous state, to pink at a predominately crystalline state (from left to right). A third color change, orange, is illustrated in the 650°C (far right) sample.

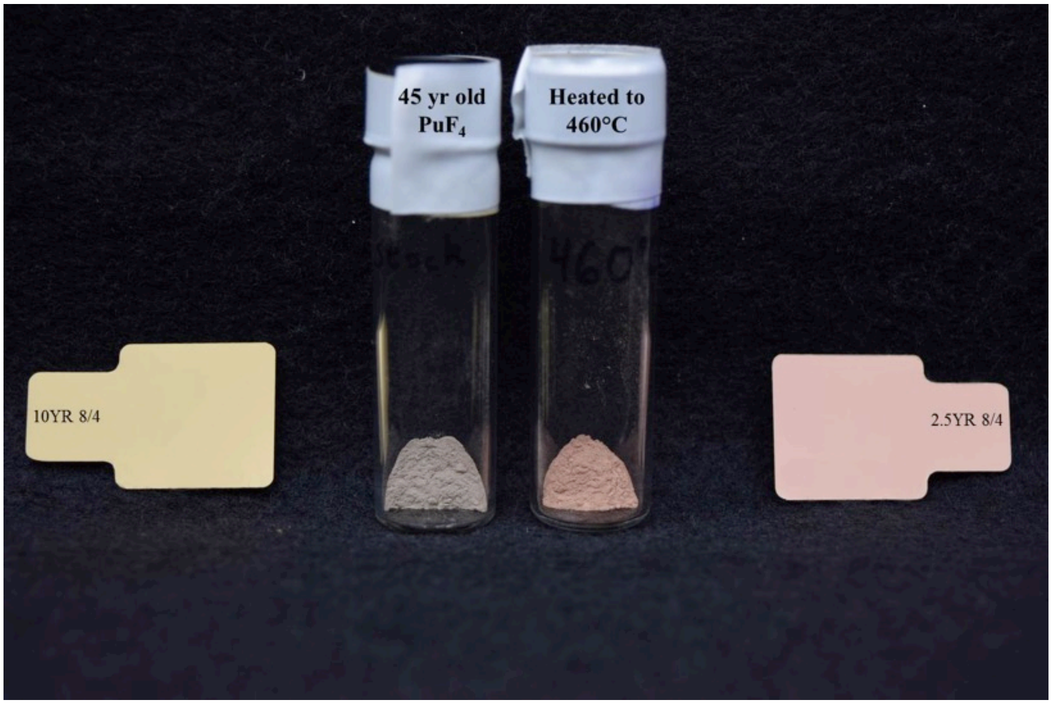

Figure 3.4 Comparison of PuF_4 that has undergone near 50 years of radiolysis (left) with that of 460°C annealed PuF_4 (right); Munsell color chart tabs are placed next to the samples for further comparison (10YR 8/4 right tab and 2.5YR 8/4 left tab).

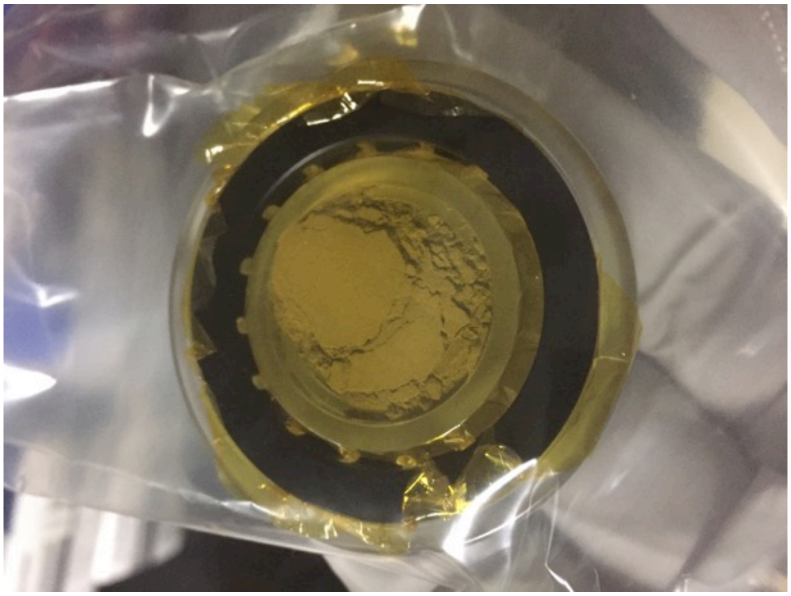

Figure 3.5 1.0g sample of 350°C annealed PuF_4 within a Bruker A100B33 X-ray diffraction specimen holder sealed with 3511 Kapton®. Clearly, 1.0g of PuF_4 was not adequate to fill the entire specimen well. Therefore, for all subsequent specimens, 0.755-inch inner diameter 1100 series aluminum washers were fit into each A100B33 well. This reduced the well's volume by near 25 percent.

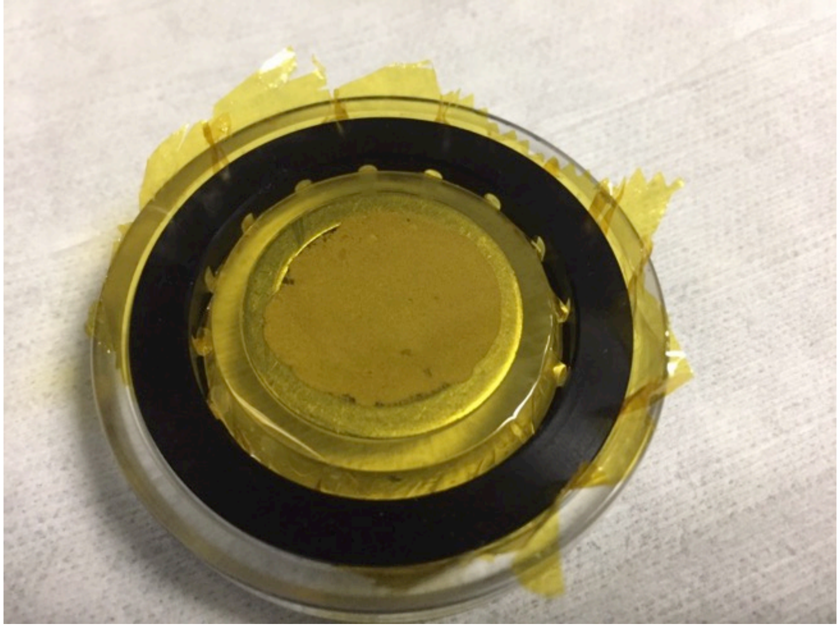

Figure 3.6 1.0g sample of 460°C annealed PuF_4 within a Bruker A100B33 X-ray diffraction specimen holder sealed with 3511 Kapton®. A 0.755-inch inner diameter 1100 series aluminum washer was fit into the A100B33 well. This reduced the well's volume by near 25 percent. This sample exhibited a more suitable surface flatness for X-ray diffraction analysis.

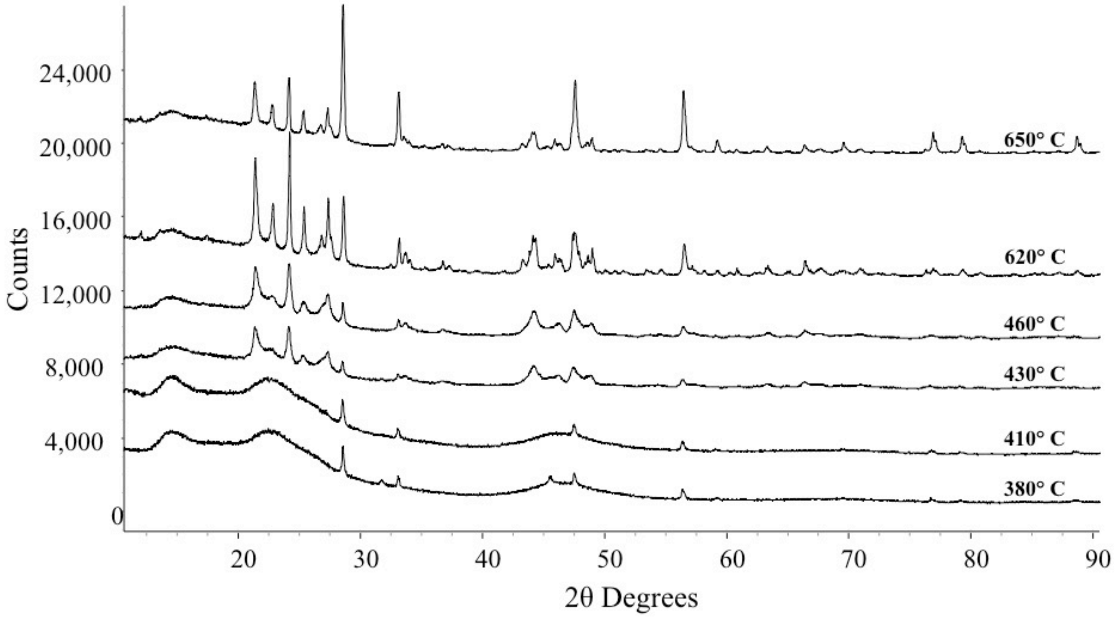

Figure 3.7 Diffraction patterns of 6-1.0g samples of PuF_4 annealed at temperatures in the 380°C-650°C range. The diffraction patterns have been vertically shifted about the y-axis for comparison. A clear transition in peak broadness at the 23° and 47° 2θ is illustrated between the sample annealed at 410°C and the sample annealed at 430°C. The reordering of plutonium tetrafluoride crystals is evident in the 20°-30° and 40°-50° 2θ regions. The ingrowth of plutonium oxide can be seen increasing above 430°C at 28°, 47.5, and 56° 2θ.

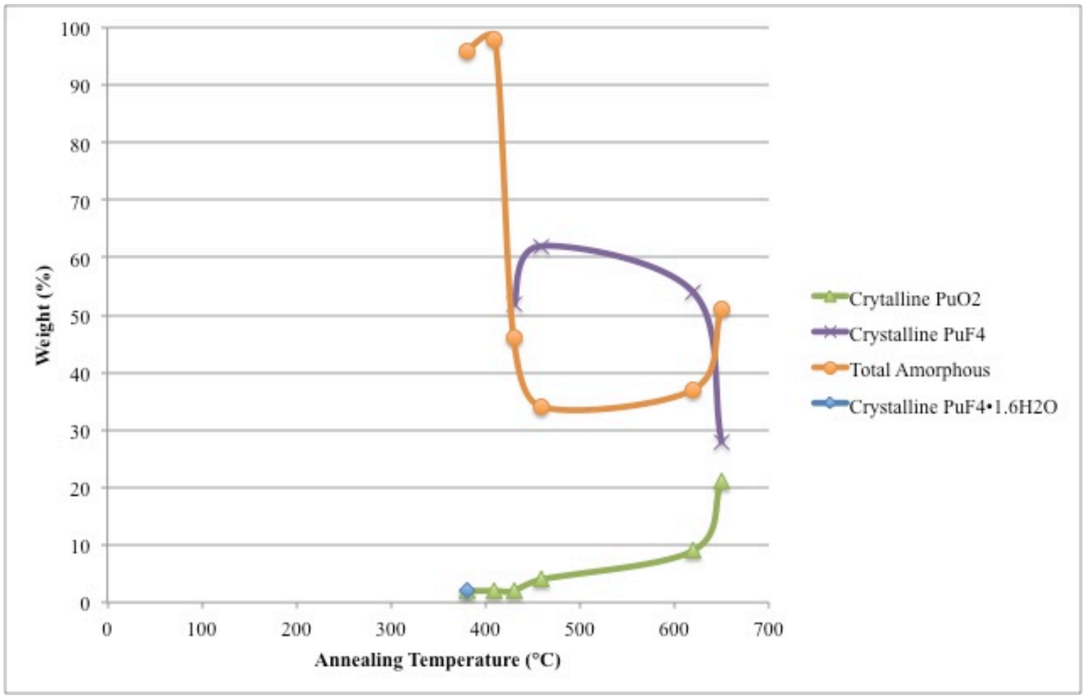

Figure 3.8 X-ray diffraction data for the 6-1gram PuF_4 samples that corresponds to Table 3.1. There is a well-defined pattern of reversal to the amorphization of PuF_4 with annealing temperatures above 430°C and below 620°C.

Table 3.1 X-ray diffraction data for the 6-1gram PuF_4 samples, normalized for amorphous and PuO_2 content with respect to annealing temperature.

Annealing Temperature (°C)	Weight % PuO_2	Weight % PuF_4	Weight % $PuF_4 \cdot 1.6H_2O$	Weight % Amorphous	Crystallite size PuF_4 (nm)	Crystallite size PuO_2 (nm)
380	2	-	2	96	-	80
410	2	-	-	98	-	76
430	2	52	-	46	14	39
460	4	62	-	34	16	48
620	9	54	-	37	60	80
650	21	28	-	51	68	93

CHAPTER 4

LONG-TERM ANNEALING OF AMORPHOUS PLUTONIUM TETRAFLUORIDE

4.1 Abstract

One of the last remaining samples of plutonium tetrafluoride that was produced at the Hanford Site's Plutonium Finishing Plant (PFP) has been analyzed at the Pacific Northwest National Laboratory (PNNL) since 2014. The plutonium has been stored within sealed containers since it was produced in the late 1960s. It has undergone metamictization through self-induced alpha radiolysis. This work reports on investigations into this metimictization, and the effect that long-term (>12 hour) annealing has on its reversal through recrystallization.

4.2 Introduction

Since 2014, samples of plutonium tetrafluoride from one of the last remaining stocks that was produced at the Hanford Site's Plutonium Finishing Plant (PFP) have been analyzed at the Pacific Northwest National Laboratory's (PNNL) Radiochemical Processing Laboratory (RPL). The plutonium tetrafluoride under study was produced before 1970 and has been stored in sealed containers since that time. There are two earlier studies linked to this work that looked at thermogravimetric/differential thermal analyses and X-ray diffraction patterns of the PFP produced plutonium tetrafluoride (*1*), (*2*). These analyses determined that the material had undergone metamictization during its approximately 50 years of storage (*1*). This metamictization was attributed to the alpha radiolysis that is inherent with plutonium and plutonium bearing materials (*1*), (*2*). Through the thermogravimetric/differential thermal analyses, it was determined that the amorphous plutonium tetrafluoride underwent an exothermic reaction upon thermal annealing within an argon atmosphere at approximately 414°C (*1*).

It was also determined during these analyses that a color change, from a brown-grey to salmon pink, accompanied some recrystallization post-reaction in the plutonium tetrafluoride (*1*). The exothermic reaction and color change have been assigned as products of the recrystallization (*1*), (*2*). The color change has been compared to a similar behavior seen in sodium chloride upon irradiation (*1*). The color change in sodium chloride has been credited to F-center formation in its crystal structure vacancies (*16*). The exothermic reaction in the plutonium tetrafluoride has been attributed to a reordering of its crystal structure, by liberation of F-center and Frenkel type defects (*1*), (*2*). The Frenkel defect mechanism is evident based on this behavior in other metamict actinide bearing compounds (*1*), (*2*), (*3*). The F-center formation is a postulation based on the high ionization rate within plutonium compounds, and this comparable color change within some alkali halides (*4*).

There is an interesting opportunity to explore the probable F-center formation in plutonium tetrafluoride and the annealing of these defects through “bleaching” with a certain wavelength or wavelength range of light as described in Tandon (*4*). However, this study is focused on the thermal annealing effects within plutonium tetrafluoride.

Based on two earlier works, three long-term (>12 hours) anneals of the amorphous plutonium tetrafluoride, one at 300°C for 24 hours, one at 350°C for 24 hours, and one at 400°C for 12 hours, were chosen for this study (*1*), (*2*). These temperatures were selected based on the possibility of a 400°C minimum temperature for the effective recrystallization of the amorphous tetrafluoride.

4.3 Background

4.3.1 Radiolysis in plutonium tetrafluoride

As previously stated, two earlier studies on this topic discussed the possible mechanisms of amorphization in plutonium tetrafluoride in comparison to those found in uranium and plutonium oxides (*1*) (*2*). It has been shown that there are similarities among the actinide oxides with regards to alpha radiation-induced crystal lattice parameter expansion (*5*). This lattice parameter expansion is a primary driver of crystal lattice damage in these compounds. The saturation point of this lattice parameter expansion has been estimated to range from approximately 0.3-0.6 percent for plutonium and uranium oxides, which correlates to a crystallite volume increase of near 1.0 percent (*5*). This saturation point is reached in plutonium oxide at roughly 10 years post-production (*4*).

Radiolysis in plutonium tetrafluoride is expected to follow a similar time line as that in plutonium oxide. Crystal lattice damage is certainly evident in the near 50-year-old Hanford produced plutonium tetrafluoride. Samples of this plutonium are amorphous according to multiple X-ray diffraction analyses (*1*) (*2*). The mechanism of that amorphization has been proposed to be self-induced alpha radiolysis (*1*) (*2*). In uranium and plutonium oxides, Frenkel defects cause crystal lattice parameter expansion according to a model that has been reported by Nellis et al. (6) and expanded upon by Weber (7). This type of crystal lattice expansion has not been seen in plutonium tetrafluoride (1) (2). However, Frenkel defect formation is the logic primary mechanism of amorphization in plutonium tetrafluoride. As previously mentioned, the speculated F-center-induced color change is seen as a byproduct of these Frenkel defect formations and ionization mechanisms (2); however, the exact nature and speed of this radiolysis in plutonium tetrafluoride has yet to be determined.

4.3.2 Mechanisms of annealing

If plutonium tetrafluoride does not follow the radiolytically induced crystal lattice expansion model of the actinide oxides, then a question must exist on whether plutonium tetrafluoride follows the same annealing behavior of the actinide oxides. It has been shown that uranium oxide, plutonium oxide, and even the lanthanide, cerium oxide, undergo a crystal structure reordering in multiple phases during the annealing process (*7*). This reordering reduces the crystal lattice parameter expansion induced by radiolysis (*7*). Furthermore, the mechanisms of this recrystallization are shown to be primarily defect clustering, interstitial-vacancy recombination, helium liberation, and F-center-molecule recombination (*2*). An approximation of the two-stage recrystallization curve for polycrystalline plutonium oxide annealed for 18 hours is shown in Figure 4.1 (*7*). Single crystal plutonium oxide has been demonstrated to follow a three-stage trend (*7*).

Figure 4.2 compares the curve from Figure 4.1 with that of short-term (<1 hour) annealing data on plutonium tetrafluoride (*2*) (*7*). Figure 4.2 displays a noteworthy trend between the reduction in total amorphous content within the plutonium fluoride from (*2*) and the radiolytically damaged plutonium oxide data from (*7*), as annealing temperatures are increased. The slope and temperature range of the curves appear to show a relationship in the 400°C-450°C range. This trend is near the 414°C exothermic reaction recorded during plutonium tetrafluoride recrystallization experiments in 2015 and 2016 (*1*). The trend might relate to the activation energy of Frenkel cation defect reordering since plutonium fluoride and dioxide both contain an equal cation, Pu^{4+} (*8*).

The activation energy equation that Weber reported for the plutonium oxide reordering data (7) is:

$$E_0 = kT\ln(Ct) \qquad (1)$$

where:

E_0 –activation energy of recrystallization (eV)

k – Boltmann constant (eV/K)

T – absolute annealing temperature (K)

C – frequency factor (also called pre-exponential factor) (-s)

t – annealing time (s)

The frequency factor, *C*, is reported to be 10^{10} (s^{-1}) for annealing studies of plutonium, uranium, and cerium oxides along with calcium, barium, and strontium fluorides (*7*). Therefore, 10^{10} (s^{-1}) is a logical choice for the estimations with plutonium fluoride shown in Figures 4.3 and 4.4. Figure 4.3 displays activation energy values in the tetrafluoride based on isochronal annealing at 1, 10, and 100 minutes at the absolute annealing temperature shown on the x-axis. Weber estimated the activation energy values for plutonium oxide annealed at 30 minutes. The values of his estimations are shown along with the plutonium tetrafluoride data in Figure 4.3. Figure 4.4 displays activation energy values in plutonium tetrafluoride based on isothermal annealing at 325°C, 380°C, 410°C, and 430°C degrees for the durations shown on the x-axis.

The agreement between plutonium tetrafluoride and oxide activation energy estimations shown in Figure 4.3 is logical due to the simplicity of Eq. 1 and the shared value of the frequency factor. The experimentally estimated activation energy for anion vacancy migration in plutonium dioxide has been reported to be 0.5 eV (*7*). Furthermore, Weber postulated that the value of oxygen interstitial migration was 1.9 eV based on 0.5 hour anneals of plutonium dioxide at 450°C (*7*). The migration of oxygen interstitials has been taken to be the first stage of defect reordering in the oxide (*7*).

The second stage of defect reordering in plutonium oxide has been estimated to take place at 675°C during a 0.5 hour anneal (*7*). This is estimated to encompass the migration of cation vacancies (*7*). The activation energy for the second stage has been estimated by Weber to be 2.5 eV (*7*). These values presented by Weber show some agreement with the previous short-term annealing studies with plutonium tetrafluoride (*1*) (*2*). The activation energy for significant defect reordering in plutonium tetrafluoride, and therefore recrystallization, appears to be near 1.5eV in the 400°C range (*1*) (*2*). This would also be in the range of activation energies reported by Weber for reordering in cerium and uranium oxides (*7*). However, this is certainly a gross comparison of the activation energies of each compound.

During the short-term study, there appeared to be temperature limitations on the annealing of plutonium tetrafluoride if the ingrowth of plutonium dioxide is a concern

(*2*). An argon cover gas has been used in previous studies to limit this ingrowth (*1*) (*2*). However, if the stage-two cation vacancy migration temperature of 675°C reported by Weber is required for this same behavior in plutonium tetrafluoride, the gas flow rates used in the earlier studies do not appear sufficient to maintain its stability (*1*) (*2*). Clark et al. reported that plutonium tetrafluoride is stable in oxygen up to 600°C (*8*). However, Cleveland reported that plutonium tetrafluoride is unstable above 300°C in moist air, with a complete conversion to dioxide at 600°C (*9*). Cleveland's report appears to be more inline with current data (*1*) (*2*).

The lack of color change data with the radiolysis and annealing of plutonium oxide is an interesting note. As can be seen in Figure 4.5, there is a significant color change in plutonium tetrafluoride annealed above 400°C. The initial studies with the compound have shown that the color change is present with reductions in the amorphous content (*1*) (*2*). This is a discrepancy between the two compounds and warrants further investigation.

4.4 Experimental approach

4.4.1 Long-term annealing

Four approximately 1.0g plutonium tetrafluoride samples were annealed for 12 hours or more within a MTI Model KSL-1100X muffle furnace at PNNL. The furnace is contained within a glovebox at PNNL's Radiochemical Processing Facility (RPL). The MTI Model KSL-1100X muffle furnace chamber volume is 1 liter. The atmosphere within the furnace was purged with argon gas at a rate of approximately 5 liters per minute. Each sample was split into 0.5g batches to increase the surface area available for reaction. Each 0.5g batch was contained within a 10.0 ml magnesium oxide crucible with a loose-fitted magnesium oxide lid. The loose-fitted lids were used to ensure that an adequate flow of argon reached the plutonium tetrafluoride within each crucible. Figure 4.5 illustrates a pre-annealed and post-annealed 0.5g batch of plutonium tetrafluoride within a magnesium oxide crucible.

Short-term (<1 hour) annealing of plutonium tetrafluoride has previously been performed at 350°C, 380°C, 410°C, 430°C, 460°C, 620°C, and 650°C (*2*). The data from these short-term anneals showed that above 400°C and below 460°C, recrystallization of plutonium tetrafluoride proceeded without significant ingrowth of oxides (*2*). Above 460°C, there appeared to be a significant ingrowth of oxides (*2*), and below 400°C, recrystallization of the compound does not appear to occur in the short-term (<1 hour) (*2*). These results were the basis for selecting long-term (>12 hours) annealing times for this study. 4-1.0g samples were annealed according to Figure 4.6. The temperature data was collected from a calibrated Omega Type K thermocouple within the furnace chamber. A J-KEM thermocouple reader and over-temperature control was used with J-KEM data logging software to capture the data on a laptop that was external to the glove box.

Once each anneal was complete, the samples were stored within 20ml glass vials under an air atmosphere until the X-ray diffraction specimens were prepared.

4.4.2 X-ray diffraction analyses

Bruker A100B33 X-ray diffraction specimen holders were used with each set of annealed plutonium tetrafluoride. A 0.755-inch inner diameter 1100 series aluminum washer was fit into each A100B33 well in order to reduced the A100B33's well volume by near 25 percent. This reduction in the well's volume ensured that 1.0g of plutonium tetrafluoride provided a suitable specimen surface height and flatness. 3511 Kapton® was used to seal the plutonium powder onto the specimen holder. Silicon grease was placed within the A100B33 snap ring well to trap loose plutonium particles. Figure 4.7 illustrates the Bruker specimen holder with Kapton® and 1.0g of plutonium tetrafluoride.

The samples were analyzed with a Rigaku Ultima IV powder X-ray diffractometer located within the RPL. The diffractometer used a 40kV, 40mA Cu X-ray tube, a D/teX linear position sensitive silicon strip detector, and a 285mm radius vertical θ/θ goniometer. An Eulerian cradle with automated sample height adjustment and sample rotation was also used. The instrument ran an automated sample alignment routine that adjusted the sample height to the proper position prior to data collection. A nickel filter was used to reduce the amount of diffracted kβ X-rays observed.

Full pattern Rietveld refinement was performed using the TOPAS v5 Bruker software package. Fundamental parameter type peak shapes were used in the refinement. The instrument contribution to peak broadening was determined by fitting three functions to a Lorentzian function with 1/cos(θ) dependence, a hat function and a circles function with 1/tan(θ) dependence, to a SRM 640d diffraction pattern standard supplied by the National Institute of Standards and Technology (NIST). The split settings for both the NIST standard and plutonium samples were equal. The instrument zero error was determined using the NIST SRM 640d. The crystallite size reported was determined using the Double-Voigt approach as implemented in the TOPAS v5 (Bruker) software package (*10*). The crystallite size reported was from the peak integral breadth of the Lorentzian type convolution to the peak shape, with an assumption of spherical crystallites. The background was modeled with a first order Chebychev polynomial 1/x function. Quantification was performed with a external standard method developed by O'Conner et al. (*11*) and Jansen et al. (*12*) that used a NIST SRM 676a standard, analyzed within a Bruker specimen holder and Kapton® identical to that of the plutonium samples.

Previous studies refined the unit cell parameters of a 620°C annealed sample of plutonium tetrafluoride from Zachariasen's structure of neptunium tetrafluoride (*1*) (*2*) (*13*). The 620°C sample was chosen for its comparative crystallite size to Zachariasen's structure (*13*). The refined unit cell dimensions chosen for these analyses was a = 12.6074 (7) Å, b = 10.6408 (6) Å, c = 8.2447 (5) Å, β = 126.328 (4)°. Plutonium dioxide was also used to model the observed diffraction patterns (*14*). Figure 4.8 illustrates the diffraction patterns for the 3 of the 1.0g samples (from 300°C-400°C) annealed for 24 hours, vertically shifted about the y-axis for comparison. Figure 4.9 illustrates the diffraction pattern of the 1.0g sample annealed for 12 hours from 400°C-300°C, along with the modeled patterns for plutonium tetrafluoride and plutonium dioxide. The contribution from the Kapton® is shown in Figure 4.10, as well.

As shown in Figure 4.10, Kapton® polyimide film that was used to contain each plutonium powder sample contributed to the diffraction pattern in the form of amorphous (broad) peaks at 14.933° and 18.8945° 2θ. These peaks along with broad peaks observed near 23° and 47° 2θ in the 300°C –350°C annealed samples were modeled with freely refined peaks. In the short-term annealing study, an attempt was made to use the refined plutonium tetrafluoride structure, fitted to the broad peaks observed in samples annealed at 380°C – 410°C (*2*). This was reported to not result in a satisfactory fit (*2*). Therefore, like the previous analyses, the addition of freely refined peaks allowed for an more accurate calculation of known phase peak areas in the presence of unknown amorphous components (*2*).

Further refinement of the diffraction pattern included a discount for the amorphous artifact from the Kapton® film. The Kapton® film was used to analyze the 100% crystalline reference standard (SRM 676a) in the same manner as that of the plutonium samples. Therefore, it could be accounted for in the results.

4.5 Discussion

In the thermogravimetric/differential thermal analysis studies, mass loss in the Hanford produced amorphous plutonium tetrafluoride has been reported to be less than 1 percent (*1*). However, under the long-term annealing conditions, mass loss has been measured to reach near 7 percent Figure 4.10 illustrates the mass loss for each sample measured at the 0.5g batch scale.

Liberation of hydrates is a reasonable explanation for the greater mass lost over the long-term (>12 hour) annealing conditions. This is arguably confirmed with results from the short-term (<1 hour) annealing study (*2*); it was found that a plutonium tetrafluoride hydrate crystalline phase appeared within the diffraction pattern of a sample annealed for less than 10 minutes at 380°C (*2*). The hydrated species within the sample were reported to be 2 percent (*2*). If combined with the oxide ingrowth mass loss estimation from the oxide data in Table 4.1, this corresponds well to the measured mass loss data. The crystalline hydrated species was not seen in these analyses, however, as suspected in the short-term annealing study, the hydrated species could be within the amorphous content until its recrystallization (*2*).

Often, this type of mass loss coupled with the color change seen in the amorphous plutonium tetrafluoride would be linked solely to hydration. This was an initial assumption during the first work with this material (*1*). However, this assumption was abandoned once the thermogravimetric/differential thermal analyses reported an insufficient mass loss (< 1 percent) upon bleaching and recrystallization (*1*). This is contradictory to the Clark et al. report that plutonium tetrafluoride hydrate is pink, with the anhydrous being pale brown (*8*). Through experience with the anhydrous plutonium tetrafluoride and previous annealing studies, it is known that anhydrous plutonium tetrafluoride is pink and not pale brown (*1*) (*2*). Furthermore, color change in this material appears to accompany recrystallization and not only mass loss.

A portion of the mass loss can be accounted for by the exchange of fluoride anions for oxide anions due to the ingrowth of plutonium oxide within the samples. The molar mass of plutonium dioxide is approximately 86 percent of the molar mass of plutonium tetrafluoride. Therefore, if the ingrowth of oxide is assumed to be near 25 percent within a 0.5g batch, the resulting mass loss would be approximately 0.017g per batch. This equates to a 3.4 percent mass loss. Figure 4.11 illustrates the calculated mass loss values for oxide ingrowth data from Table 4.1 plus a 2 percent mass loss for dehydration. Impurities within the argon gas used to purge the furnace chamber are a logical source of oxides for anion exchange.

Figure 4.12 illustrates the reordering and oxide ingrowth data for the 300°C 12 hour, 350°C 24 hour, 400°C 24 hour, and 400°C-300°C 12 hour annealed samples. There is a clear increase in the oxide formation within the samples annealed for 24 hours, with and without significant tetrafluoride reordering. For example, the sample annealed at 400°C decreasing to 300°C over 12 hours resulted in a 12 percent mass loss of plutonium tetrafluoride recrystallization, with a 1 percent mass loss in plutonium oxide content, whereas the sample annealed at 350°C for 24 hours resulted in 0 percent plutonium tetrafluoride recrystallization, with a 12 percent by weight plutonium oxide content. The sample annealed at 400°C for 24 hours recorded over twice the recrystallization of plutonium tetrafluoride to that of the 12 hour sample but at the cost of 25 percent by weight oxide ingrowth.

Figure 4.13 illustrates the crystallite size changes of plutonium tetrafluoride and oxide with time and temperature. The data shows that the crystallite size increase of plutonium tetrafluoride is near stagnant at 11 nm and 12 nm for the 400°C-300°C 12 hour and 400°C 24 hour annealed samples, respectively. This coupled with the plutonium oxide ingrowth data from Table 4.1 and Figure 4.12 argues that short-term (<12 hour) annealing for the recrystallization of plutonium tetrafluoride is preferential if plutonium oxide ingrowth is a concern. Furthermore, based on the results of the short-term and long-term annealing studies, plutonium tetrafluoride appears to begin recrystallization at the 400°C range and above (*2*).

4.6 Conclusion

This study was focused on the recrystallization of amorphous plutonium tetrafluoride under long-term (>12 hour) annealing conditions. It serves as a compliment to prior studies focused on the mechanisms of radiolysis in plutonium tetrafluoride as it compares to plutonium dioxide, and the effect of short-term annealing on the reversal of the amorphization (*1*) (*2*). The plutonium used for these studies was part of the last remaining stock of plutonium tetrafluoride made at the Hanford Site's PFP and has been in storage for near 50 years (*1*) (*2*).

The results presented show a clear trend of oxide formation in plutonium tetrafluoride that has been annealed at temperatures in excess of 350°C for long periods of time (>12 hour) in an argon atmosphere. This is significantly lower than the stability of plutonium tetrafluoride in an inert atmosphere as reported by Clark et al. (*8*). More importantly, only the 12 hour 400°C- 300°C and 24 hour at 400°C annealed samples showed recrystallization of plutonium tetrafluoride. The 300°C and 350°C samples did not shown any reordering of the tetrafluoride. This confirms the lack of recrystallization in the samples annealed at 350°C and 380°C of the short-term annealing study (*2*). It appears that plutonium tetrafluoride requires an annealing temperature near 400°C in argon to effectively recrystallize. The activation energy in this range has been estimated to be 2 eV for initial defect migration/reordering.

4.7 Acknowledgements

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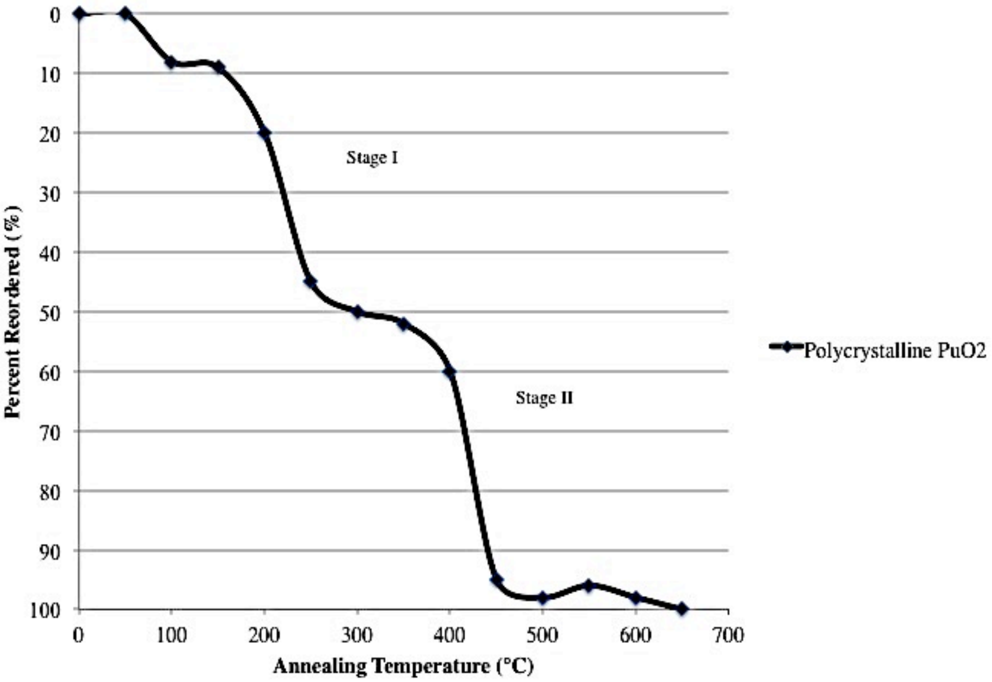

Figure 4.1 Approximation of the 18 hour annealing trend for plutonium oxide (PuO_2) given by Weber (*7*). The two-stage trend is common among the polycrystalline actinide and lanthanide oxides studies (*7*).

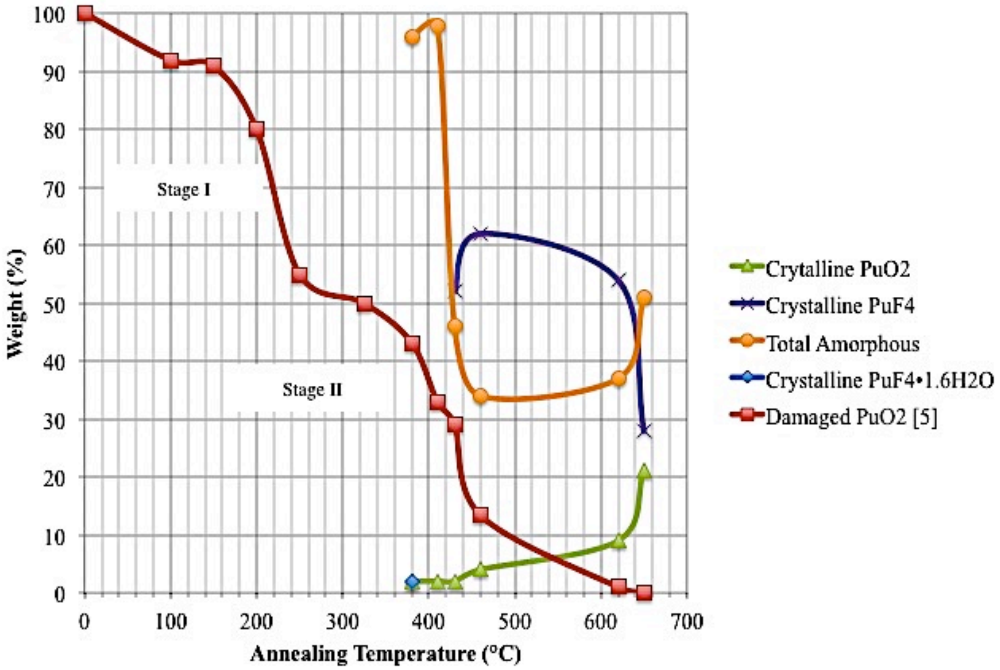

Figure 4.2 Comparison of the trends of short-term (< 1 hour) annealed plutonium tetrafluoride (PuF_4) and long-term (18 hour) annealed PuO_2. There is a clear overlap of the data in the 400°C-450°C annealing range. This region agrees well with the 414°C exothermic reaction during PuF_4 recrystallization reported by differential thermal analyses in an earlier work (*1*).

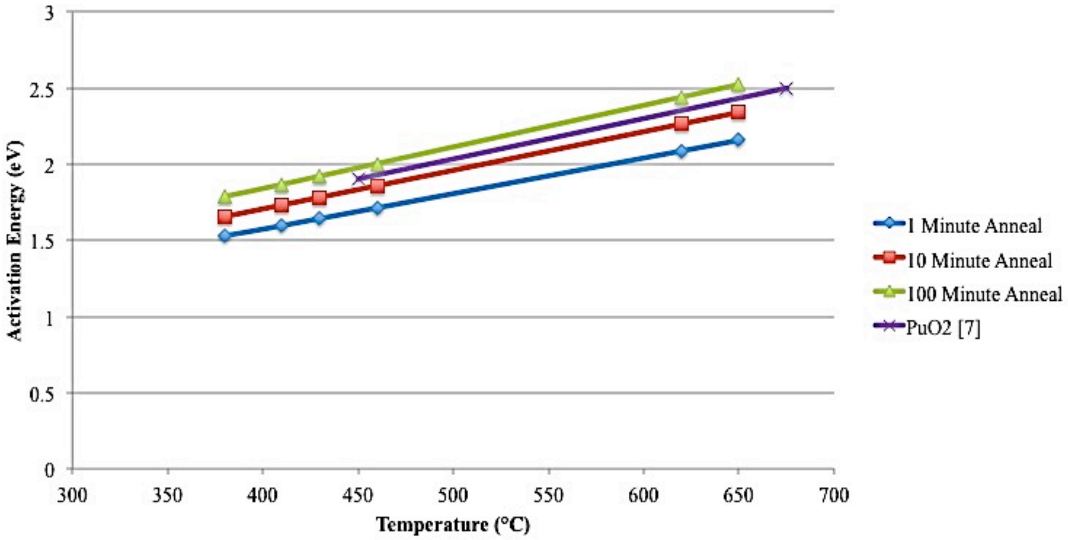

Figure 4.3 Activation energy estimations in PuF_4 calculated with Eq. 1 (*7*). The isochronal annealing curves were chosen at 1, 10, and 100 minutes based on Weber's work with PuO_2. The values clearly lie within 1.5-2.5 eV and agree well with the estimation by Weber (*7*).

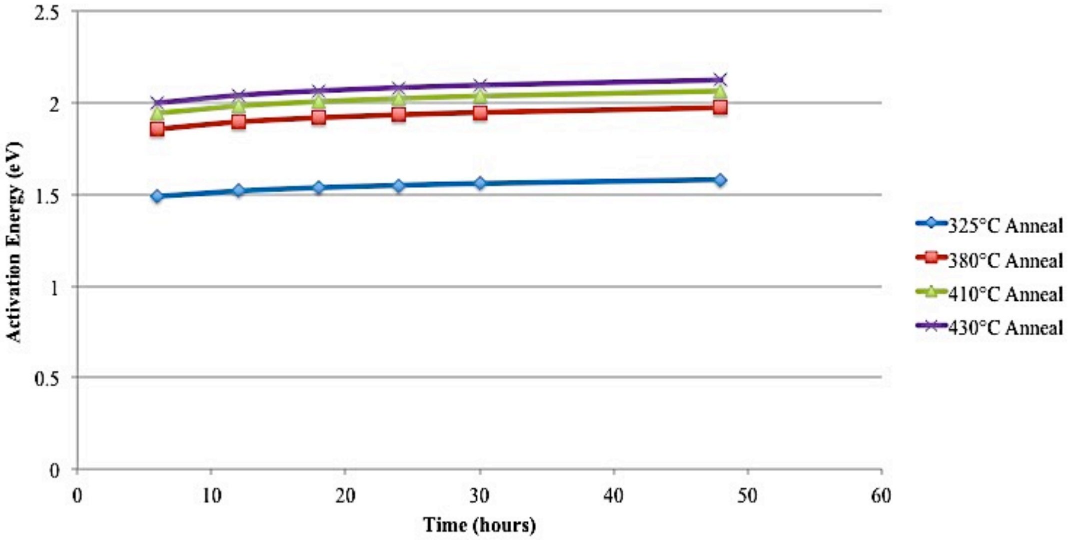

Figure 4.4 Activation energy estimations in PuF_4 calculated with Eq. 1 (*7*). The isothermal annealing temperatures were chosen based on the short-term annealing work in (*2*). The values are inline with Figure 4.3 and lie within 1.5-2.5 eV.

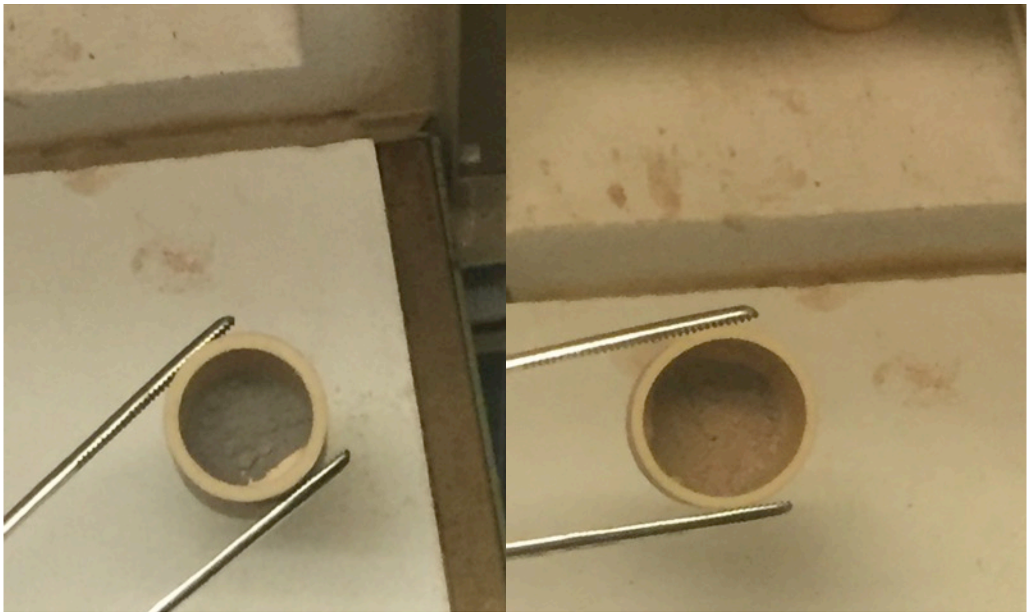

Figure 4.5 Pre-annealed (left) and post-annealed 400°C (right) PuF_4 within magnesium oxide crucibles; the PuF_4 annealed at <400°C have not displayed the color change seen in the >400°C annealed samples. The salmon pink color is typical for freshly fluorinated and >400°C annealed PuF_4. The approximately 50-year-old amorphous Hanford PuF_4 stock displays the grey color.

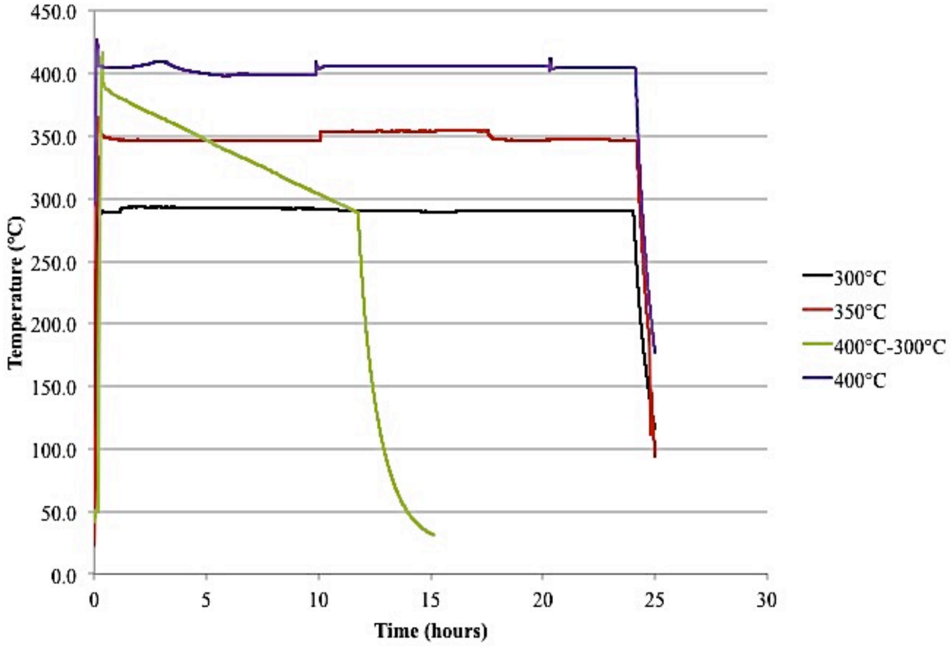

Figure 4.6 Annealing rate curves for 4-1.0g PuF_4 samples in MTI KSL-1000X muffle furnace purged with argon gas at 5 liters per minute. The PuF_4 samples were left under an argon atmosphere until a temperature below 100° was reported by the J-KEM software.

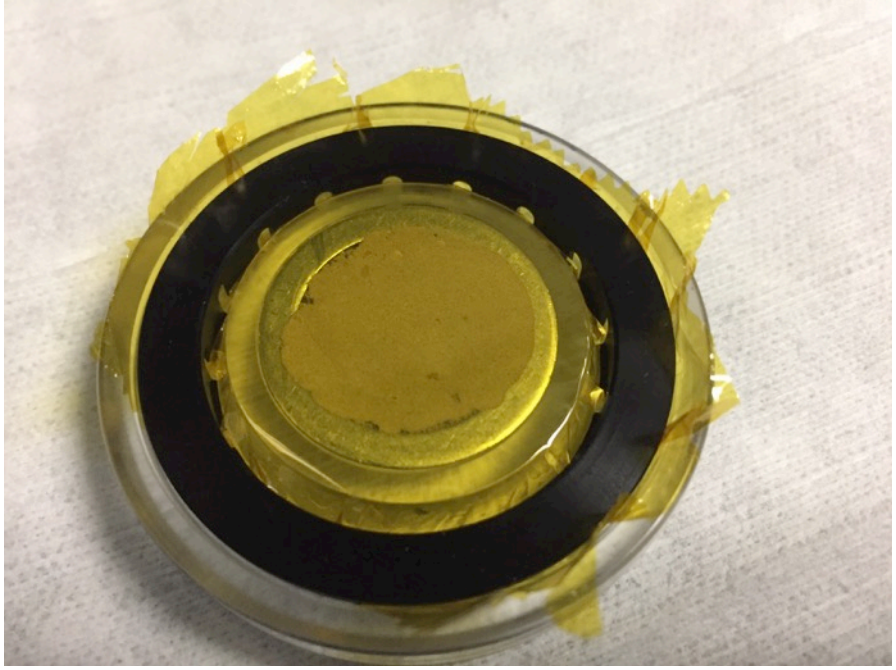

Figure 4.7 1.0g sample of 350°C annealed PuF_4 within a Bruker A100B33 X-ray diffraction specimen holder sealed with 3511 Kapton®. A 25 percent reduction in the well volume of the A100B33 was accomplished with the fitment of a 0.755-inch inner diameter 1100 series aluminum washer. This ensured that the 1.0g sample exhibited a more suitable surface flatness for X-ray diffraction analysis.

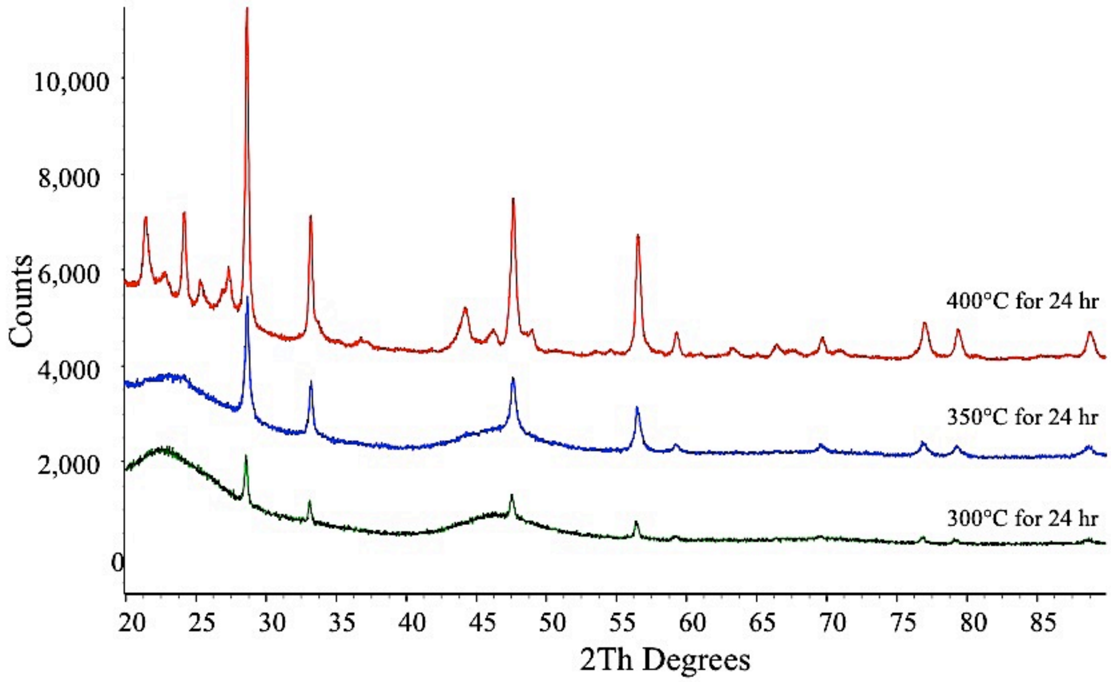

Figure 4.8 Diffraction patterns of 3-1.0g samples of PuF_4 annealed for 24 hours at temperatures in the 300°C-400°C range. The diffraction patterns have been vertically shifted about the y-axis for comparison. A clear transition in peak broadness at the 23° and 47° 2θ is illustrated between the sample annealed at 350°C and the sample annealed at 400°C. The reordering of plutonium tetrafluoride crystals is evident in the 20°-30° and 40°-50° 2θ regions. The ingrowth of plutonium oxide can be seen increasing above 300°C at 28°, 47.5, and 56°- 88° 2θ.

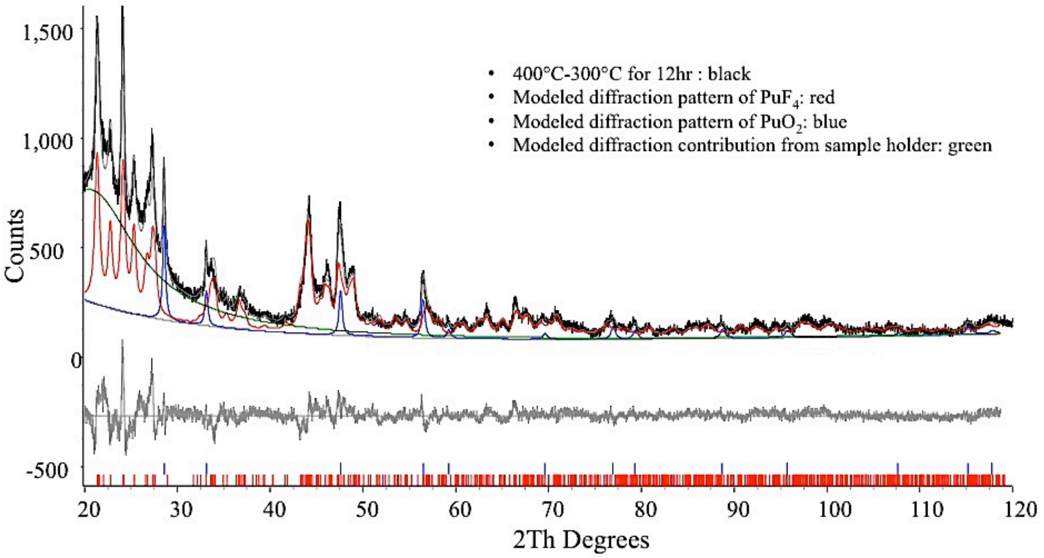

Figure 4.9 Diffraction pattern of the 400-300°C 12 hour annealed sample (black), modeled PuF_4 (red), modeled PuO_2 (blue), and Kapton® artifact (green). The reordering of plutonium tetrafluoride crystals is evident in the 20°-30° and 40°-50° 2θ regions. The ingrowth of plutonium oxide can be seen at 28°, 47.5, and 56°- 88° 2θ regions.

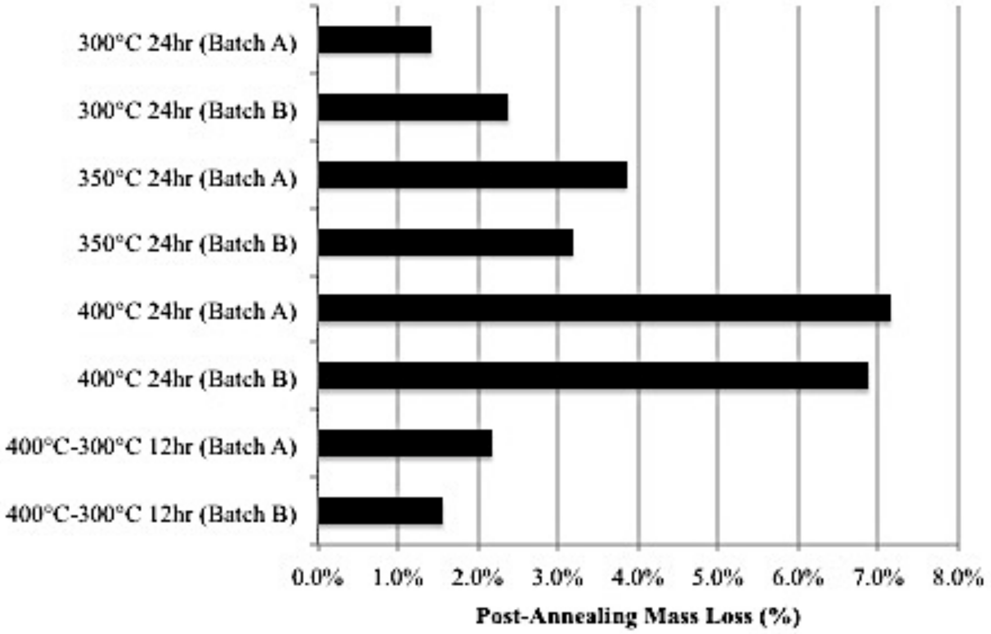

Figure 4.10 Mass loss data for each PuF_4 sample measure at the 0.5g batch scale. The graph clearly illustrates that the mass loss in the Hanford produced amorphous material is dependent on time at the maximum annealing temperature.

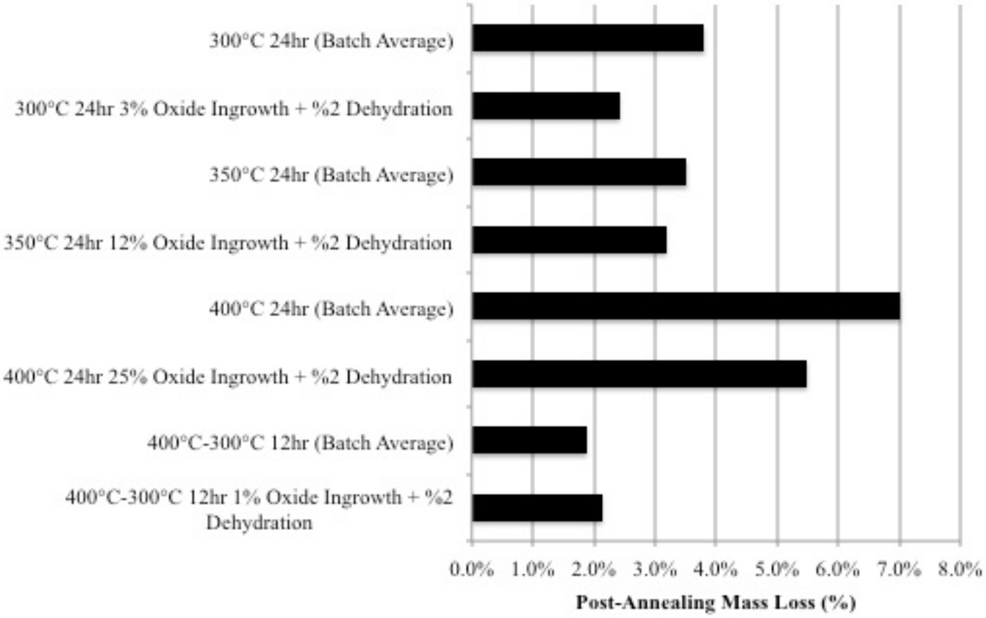

Figure 4.11 Mass loss comparison of batch average mass loss to estimations for PuO_2 ingrowth and dehydration by weight percent. There is a clear correlation between the ingrowth of PuO_2 and mass loss seen in the batches from Figure 4.9. The 2 percent additional mass loss on each oxide ingrowth bar does not fit blindly with the long-term annealing data.

Table 4.1 X-ray diffraction data for the 4-1.0g PuF_4 samples, normalized for amorphous and PuO_2 content with respect to annealing temperature and time.

Annealing Temperature (°C)	Weight % PuO_2	Weight % PuF_4	Weight % PuF_4•$1.6H_2O$	Weight % Amorphous	Crystallite size PuF_4 (nm)	Crystallite size PuO_2 (nm)
PuF_4-300C-24hr	3	-	-	97	~1	36
PuF_4-350C-24hr	12	-	-	88	~1	18
PuF_4-400C-24hr	25	35	-	41	12	29
PuF_4-400C-300C-12hr	1	12	-	87	11	18

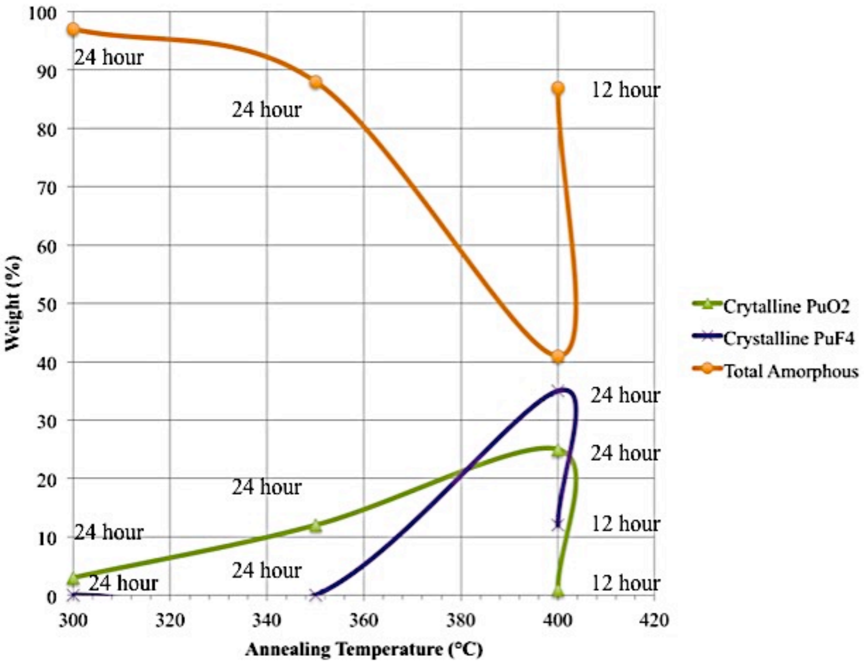

Figure 4.12 X-ray diffraction data for the 3-24 hour and 1-12 hour annealed 1.0g PuF_4 samples that correspond to Table 4.1. There is a well-defined pattern of reversal to the amorphization of PuF_4 with annealing temperatures above 300°C. Clearly, the 12 hour at 400°C-300°C annealed sample contained significantly less PuO_2 ingrowth while also less PuF_4 crystallinity.

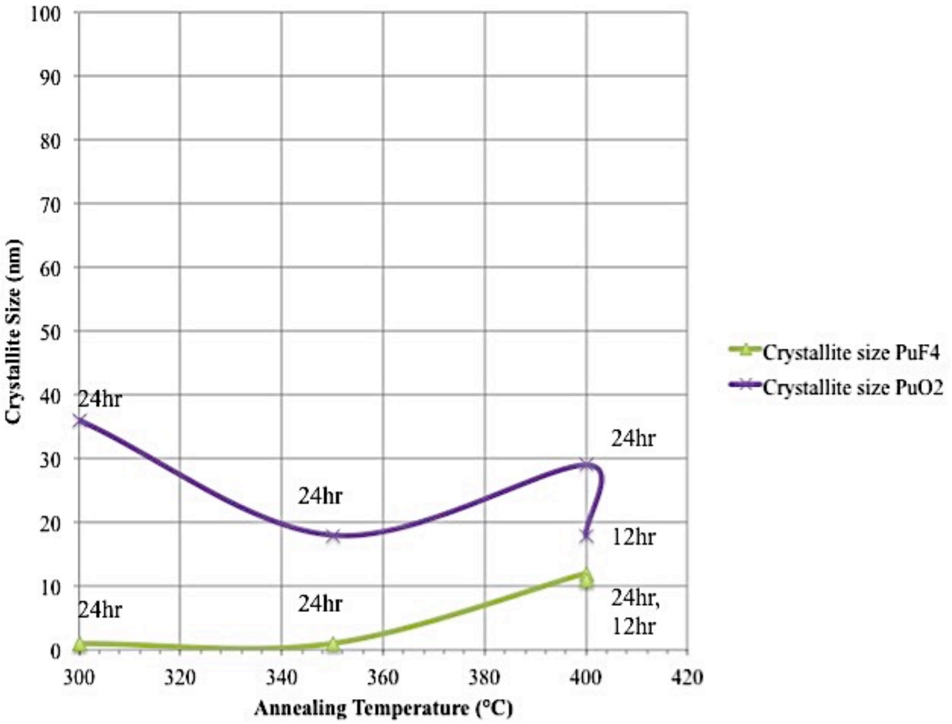

Figure 4.13 Crystallite size comparison of 12 hour and 24 hour annealed 1.0g PuF_4 samples. The crystallite size of PuO_2 appears to follow a parabolic curve during 24 hour anneals from 300°C-400°C, with a near equal crystallite size for 12 hour 400°C-300°C and 24 hour 350°C anneals. PuF_4 crystallite size appears to grow with temperature.

CHAPTER 5

CONCLUSION

There is limited information on the behavior of plutonium tetrafluoride, as it is rarely reported on by civilian industry. However, with the resurgence of all-metal nuclear fuels and some advanced fast nuclear reactor fuels, there is a need to investigate the nuances of working with plutonium tetrafluoride. In contrast, information on plutonium oxide is much more available due to its use as a mixed-oxide fuel. However, with all plutonium compounds becoming more precious as the years of ceased plutonium production increases, plutonium tetrafluoride will need to be investigated for its stability under long-term storage conditions.

It has been shown that radiolytic damage effects plutonium tetrafluoride through self-induced alpha radiolytic amorphization. A color change from pink to grey-brown is evident once the plutonium tetrafluoride is amorphous. It has also been shown that thermal annealing can initiate the recrystallization of amorphous plutonium tetrafluoride at temperatures near 400°C. Furthermore, this recrystallization is accompanied by an exothermic reaction and color change back to pink.

However, there is a significant risk of oxide ingrowth within the plutonium tetrafluoride given annealing temperatures are above 430°C in an inert flowing gas.

Furthermore, the crystal lattice damage and annealing effects in plutonium tetrafluoride do not appear to follow the crystal lattice expansion behavior in plutonium oxide, even though the crystal lattice defect formation could be shared among the compounds. The crystallite size of plutonium tetrafluoride grows with temperature whereas the crystallite size in plutonium oxide follows a more parabolic trend.

CHAPTER 6

FUTURE WORK

There are a few questions that remain post completion of this study. Two of these questions will be the target of future work with amorphous plutonium tetrafluoride and they are:

1) Is the color change in amorphous to recrystallized plutonium tetrafluoride possible with certain wavelengths of light?
2) Is the ingrowth of oxide within plutonium tetrafluoride annealed above 430°C due to impurities in the argon gas or within the tetrafluoride? And does annealing within a vacuum or a purer/different inert gas still produce this ingrowth of oxide?

The first question could be investigated by attempting to bleach the amorphous tetrafluoride within an X-ray fluorescence device equipped with various wavelength filters. The sample preparation method that was used for the X-ray diffraction analyses in this study could be used for the bleaching work. This would allow for a non-radioactive device to be used.

The second question could be investigated by heating the amorphous plutonium tetrafluoride within a vacuum-annealing furnace. Helium could also be used as another inert gas option, and hydrogen fluoride gas could be used to baseline the process/oxide ingrowth as it is used in the production of the tetrafluoride with oxygen.