Aging of Plutonium and Its Alloys

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L ike other reactive materials, plutonium ages with time. In moist air, it "rusts" much more profusely than iron, and when exposed to other atmospheric envi- ronments, it will react to form several surface-corrosion products. In other words, plutonium ages from the outside in. What makes plutonium really special, however, is that it also ages from the inside out. As a result of its radioactive nature, it relentlessly undergoes self-irradiation damage throughout its volume. Con- sequently, nature's most unusual element becomes even more complex as it ages.

In the past, we were resigned to keeping plutonium from self-destructing—at least for two or three decades. Today, we are intensely interested in extending its storage life for many more decades, preferably as much as a century. The three articles that follow this introduction highlight the challenges we face in understanding aging phe- nomena in plutonium with the hope of achieving that goal.

In "A Tale of Two Diagrams" (page 244) Hecker and Timofeeva shed new light on the question of δ-phase stability. Since there is no clear understanding of the face-centered-cubic (fcc) δ-phase of plutonium, questions continue to persist about the long-term stability of this phase when it is retained to room temperature by the addition of a few atomic percent (at. %) gallium. In "Surface and Corrosion Chemistry of Plutonium" (page 252), Haschke, Allen, and Morales discuss the outside-in problem. Their article highlights the enormous importance of storing plutonium under controlled atmospheres in order to avoid potentially catastrophic events. Finally, Wolfer describes the inside-out problem in "Radiation Effects in Plutonium" (page 274) and develops the case for the most plausible scenario of damage induced by self-irradiation.

After briefly introducing the paper on phase stability and summarizing the paper on surface and corrosion chemistry, we will outline more broadly the potential microstructural effects of self-irradiation damage in plutonium.

Phase Stability

During aging, thermally activated kinetic processes are at work that constantly try to drive the solid toward equilibrium (its lowest energy state). Hence, any nonequi- librium structures are subject to change during aging. One of the greatest concerns about the structural integrity of plutonium and its alloys is phase stability because of the large volume changes that accompany phase changes. Hence, much work has been done over the years to determine the equilibrium phase diagrams of plutonium with most other elements in the periodic table.

However, the plutonium-gallium (Pu-Ga) phase diagram as measured by researchers in the West and in Russia showed a critical difference. The western dia-

gram shows the fcc δ-phase as the equilibrium phase at room temperature, whereas the Russian diagram shows the δ-phase decomposing to $\alpha + Pu_3Ga$ below 100°C.

The lack of agreement stemmed from the fact that kinetic processes in materials near room temperature are immeasurably slow, and so it is extremely difficult to achieve true phase equilibrium. In an effort to speed up the low-temperature kinetics, the Russians "preconditioned" their Pu-Ga alloys by transforming some of the δ-plutonium to the α'-phase. They then annealed the samples for up to 10,000 hours. The results of the experiments indicated the decomposition to $\alpha + Pu_3Ga$.

Unfortunately, the Russian work was not accepted in the West because the precise nature of the experiments was not presented in sufficient detail. The article "A Tale of Two Diagrams" provides enough detail to give the Russian work proper credibility and to make experiments that were exacting and careful known to a wide audience.

Atmospheric Surface Reactions

Although plutonium is a very reactive metal, its oxidation rate in very dry air is a minuscule 20 picometers per hour (pm/h), or less than 0.2 micrometer per year. The reason is that, much like aluminum, the plutonium metal rapidly forms, and is passivated by, a protective layer of dioxide (PuO_2) over its entire surface. However, corrosion of plutonium metal in moist air occurs at a rate 200 times greater than in dry air at room temperature and is, astonishingly, 100,000 greater at 100°C. The mechanisms of water-catalyzed corrosion of plutonium have only recently been elucidated by Haschke and coworkers. They demonstrated for the first time that hyperstoichiometric plutonium oxide (PuO_{2+x}, where x can be as large as 0.26) forms in the presence of either gaseous or liquid water. Rapid oxidation by adsorbed water produces hydrogen at the gas-solid interface and forms the higher oxide, catalyzing oxidation.

Hydrogen reacts with plutonium metal at unprecedented rates. It gains access to the metal surface by penetrating the ever-present dioxide layer at cracks or at sites where the oxide spalls, making the nucleation of the hydride reaction very heterogeneous. The hydriding rate increases exponentially as nucleation sites grow. Once the entire metal surface is covered with hydride, the reaction occurs very rapidly, and the hydride layer can grow at a rate as much as 20 cm/h linear penetration for hydrogen at atmospheric pressure. This rate is 10^{10} times faster than that of the oxidation reaction in dry air. This incredibly rapid reaction is catalyzed either by the formation of PuH or by a cubic form of the sesquioxide, Pu_2O_3. The reaction of oxygen with hydride-coated plutonium is also greatly catalyzed by PuH_x, resulting in reaction rates 10^{13} times faster than in dry air.
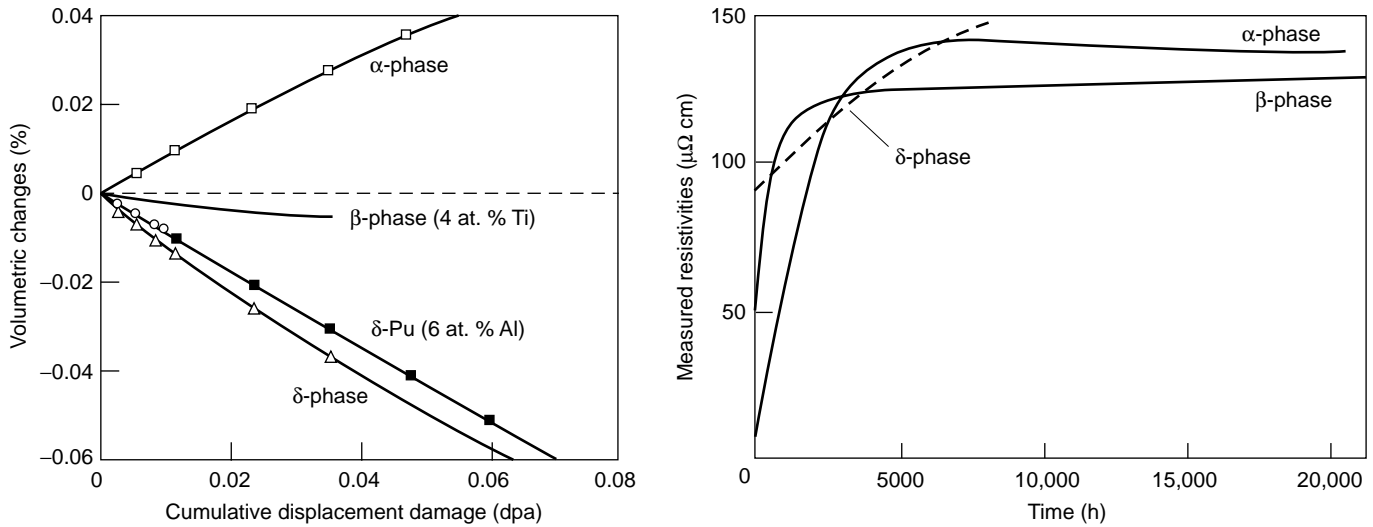
Figure 1. Volume Changes in Plutonium Resulting from Self-Irradiation at Cryogenic Temperatures

(a) The α-phase expands substantially at 4 K because Frenkel pairs are created. Whereas the β-phase shows only a slight contraction, the δ-phase shows a substantial contraction. Self-irradiation exposures were less than 0.1 dpa, which is equivalent to the damage received in 1 year. The volume changes eventually saturated at approximately 10% for the α-phase and 15% for the δ-phase. Interestingly, at saturation, the densities of all three phases appear to converge to approximately 18.4 g/cm^3, indicating that all have reached a very disordered state. (b) The damage was also monitored with electrical-resistance measurements. The electrical resistance increases for all plutonium phases of some of the same samples shown in (a). The δ-phase results are averages from several experiments.

At this time, the dramatic enhancements in corrosion rate have not been fully understood. Haschke has speculated that, under the above conditions, it is possible to get superionic transport of anions in complex crystal structures such as Pu_2O_3. Moreover, we have little fundamental knowledge, either theoretical or experimental, about how oxygen or hydrogen adsorbs on plutonium surfaces, nor do we understand the effects of alloying or defect structure in the plutonium substrate. The potential influence of electronic effects is also poorly understood. It is therefore time to turn the new surface techniques developed by the surface science community over the past 20 years to the study of interfacial reactions in plutonium.

One additional peculiarity of plutonium metal deserves mention, namely, its pyrophoricity. Plutonium ignites spontaneously in air at 500°C, but plutonium particulates, such as powder or machining chips, are known to ignite at temperatures as low as 150°C to 200°C. Martz and Haschke have shown that low-temperature pyrophoricity is caused by the formation of Pu_2O_3 followed by a rapid oxidation to PuO_2, which causes a thermal spike to the self-ignition temperature.

The above-mentioned surface reactions greatly impact plutonium handling and storage procedures. As a result, it is imperative that plutonium be protected in sealed containers without the presence of hydrogenous materials. The reason for excluding such materials is that their radiolysis, resulting from the α-decay of plutonium, will make hydrogen available, which can have catastrophic consequences.

Self-Irradiation Effects

The radioactive nature of plutonium presents an interesting interplay between nuclear and electronic processes. The unstable plutonium nucleus decays principally by α-decay[1]. The decay event produces two energetic nuclear particles—an α-particle and a recoil uranium nucleus. These particles are created in much less than a femtosecond (10^{-15} second). They share the energy released by the decay and are propelled through the crystal lattice.

The α-particle has an energy above 5 million electron-volts (MeV) and a range of approximately 10 micrometers in the plutonium lattice. It captures two electrons from the plutonium metal and comes to rest in the lattice as a helium atom. The light

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[1]The isotope plutonium-241 decays by β-decay (with a half-life of 12.3 years) to americium-241, which decays to neptunium-237 by α-decay (with a half-life of 433 years).

α-particle loses nearly 99.9 percent of its energy to electrons, heating the plutonium lattice. Some atomic displacements occur near the end of the range, producing "self-interstitial" plutonium atoms that come to rest in the interstices of the plutonium lattice and vacancies (the holes in the lattice left behind by the displaced plutonium atoms). These defects—the vacancies and the self-interstitials—are called Frenkel pairs.

The heavier uranium nucleus carries approximately 85 kilo-electron-volts (keV) of the decay energy, and it converts nearly three-quarters of its energy into atomic displacements. Its recoil triggers a complicated "ballistic"-collision cascade, which causes most of the initial damage to the plutonium lattice. The range of the uranium recoil atom in the plutonium lattice is approximately 12 nanometers. In the article "Radiation Effects in Plutonium" (page 274), Wolfer calculates the expected damage for the isotopic mix of plutonium typical of weapons stockpiles. Each uranium/helium damage cascade interacts with approximately 20,000 plutonium atoms. Most of these atoms (90 percent) are thermally excited at their lattice position, and only a small fraction (10 percent) are displaced, resulting in the generation of roughly 2500 Frenkel-pair defects per decay event. The large displacement and relaxation of plutonium atoms results in every plutonium atom being displaced, on the average, once every 10 years (or, in the units commonly used, 0.1 displacements per atom/year (dpa/yr).

The violent events of the primary nuclear-particle decay and the resulting collision cascade are followed by a local thermal spike persisting for at least picoseconds, during which additional reconfiguration of the defect structure (recombination, migration, and agglomeration) takes place. The interactions of these surviving defects with the microstructure and their evolution as a function of time and temperature determine the extent of self-irradiation effects on the properties of plutonium. Theoretical modeling using a special form of the Monte Carlo method (called kinetic Monte Carlo) provides us with insight into these important atomistic processes.

General Lattice Damage. Vacancies and interstitials affect material properties because they perturb the atomic interactions in solids. Vacancies induce lattice softening because of the missing atomic interaction at the vacancy site. Self-interstitials cause very large lattice perturbations and local stress fields. Both types of damage lead to changes in the effective atomic volumes of the lattice. In most metals, such defects affect macroscopic properties such as elastic constants, density, lattice parameters, electrical resistivity, strength, and ductility. In plutonium, we expect these to be large because the 5f electrons sit on the knife-edge between bonding and localization. It is easy to imagine that changes in atomic volume or internal stresses resulting from irradiation-induced defects could affect the delicate balance of phase stability in plutonium.

Surprisingly little research has been done into plutonium self-irradiation at ambient temperature. So far, electronic-structure calculations have been unable to deal with defect structures adequately. There are also very few systematic experimental observations. At ambient temperature, there is a very complex interplay between damage and annealing (or healing). The residual damage depends greatly on the mobility of the defects, their interactions with each other, and their interactions with other defects and solutes.

Most experiments on self-irradiation damage in plutonium have been conducted at cryogenic temperatures, at which little annealing occurs. But subsequent annealing studies looked into defect mobilities and recovery of lattice damage. As shown in Figure 1(a), the α-phase expands significantly at 4 kelvins during self-irradiation. The δ-phase (retained by alloying with several atomic percent aluminum) contracts substantially, whereas the β-phase (retained by alloying with titanium) contracts slightly. In all three cases, the electrical resistivity increased markedly during
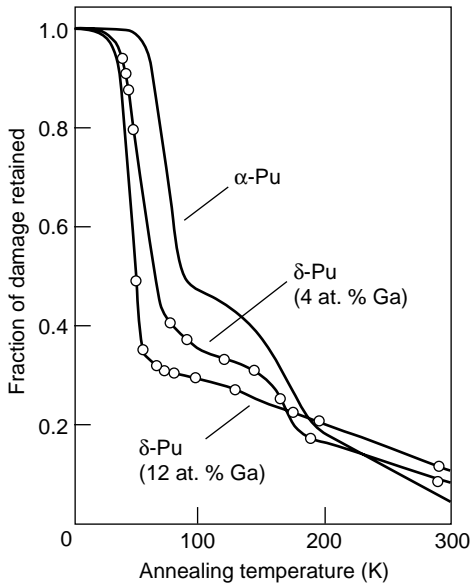
Figure 2. Recovery of Self-Irradiation Damage
Self-irradiated α- and δ-plutonium recover most of the lattice damage introduced at 4.5 K. The fraction of damage retained is measured by the fractional change in electrical resistance recovered when the samples are annealed isochronally (for short periods) as the temperature is warmed back up from 4.5 K. Most of the damage is recovered by room temperature. The α-phase sample was held at 4.5 K for 640 hours, the Pu-Ga alloy (12 at. % gallium) for 665 hours, and the Pu-Ga alloy (4 at. % gallium) for 920 hours.

self-irradiation (reflecting the generation of lattice defects) as seen in Figure 1(b). If self-irradiation is allowed to proceed long enough, all three phases appear increasingly disordered, perhaps approaching an amorphous state, converging at a density of 18.4 grams per cubic centimeter (g/cm^3).

Data from a typical annealing study (Figure 2) show that much of the damage is annealed out by 100 kelvins and most of it is annealed out at room temperature. Because of insufficient data, key parameters such as the mobility of self-interstitials and vacancies cannot be determined. However, we know that these mobilities scale with the homologous temperature (the temperature divided by the melting temperature of the material), so a comparison with other metals irradiated inside accelerators or reactors provides us with useful insight. Specifically, we estimate that self-interstitials are mobile at temperatures above 20 kelvins. Vacancies begin to migrate and annihilate near 200 kelvins, and both interstitial and vacancy clusters dissociate thermally above 400 kelvins, resulting in the complete recovery of lattice damage.

Based on our current rudimentary understanding of these processes, we cannot preclude the possibility of the continued accumulation of radiation damage in plutonium under typical storage temperatures. However, general observations of self-irradiation damage show no major macroscopic changes for at least 40 years—in other words, plutonium does not "crumble". There also appear to be no gross microstructural changes, such as phase changes or segregation. Early studies found a slight volume expansion in δ-phase alloys, on the order of 0.3 percent in 10 years. However, detailed microstructural examinations are needed to provide a better understanding. In particular, the power of x-ray absorption fine structure (XAFS) spectroscopy to probe the local structure in the vicinity of the plutonium and gallium atoms as the plutonium ages should be explored thoroughly.

Transmutation, Helium Bubbles, and Voids. The transmutation products resulting from α-decay—radiogenic helium and other actinide atoms—can also affect bulk properties. After 50 years of storage, weapons-grade plutonium will have grown in the following amounts of transmutation products: approximately 2000 atomic parts per million (ppm) helium, 3700 ppm americium, 1700 ppm uranium, and 300 ppm neptunium. After that length of time, a piece weighing 1 kilogram will contain nearly two-tenths of a liter of helium measured at standard conditions. Said differently, after 50 years of decay, the accumulated helium in plutonium would generate a pressure of 3 atmospheres in an equivalent empty volume!

The most important concern about the in-growth of actinide transmutation products in plutonium is their potential effect on the delicate balance of phase stability. Under equilibrium conditions, the addition of americium makes fcc δ-plutonium more thermodynamically stable, so several thousand parts per million of americium should help to further stabilize δ-phase alloys. Uranium and neptunium, on the other hand, reduce δ-phase stability. In both cases, however, the conditions present after the α-decay events are far from equilibrium and, hence, may not have the expected effects at ambient temperature.

The accumulation of radiogenic helium could affect the properties of plutonium substantially. Helium has extremely low solubility in metals because it does not bind. It diffuses rather easily through the lattice (as easily as vacancies) until it becomes trapped in one of the vacancies. The helium-vacancy clusters can migrate and coalesce, potentially forming into helium bubbles, which cause swelling. It is well known that less than 100 ppm of helium in fcc stainless steel can cause swelling or dramatic embrittlement. Wolfer concludes, however, that macroscopic swelling in plutonium as a result of helium bubbles is very unlikely at ambient temperature.

The combination of irradiation-induced lattice damage and the presence of helium atoms can cause void growth and bulk swelling without the presence of helium

bubbles. Void growth is an obvious potential consequence of vacancy migration and clustering. Void swelling has been found to be a serious problem for materials in the irradiation environment of reactors.

Reliable predictions of void swelling in plutonium are not currently possible because of a lack of fundamental knowledge of intrinsic properties such as the relaxation volumes for vacancies and interstitials. Wolfer's best estimate is that void swelling is expected to begin for δ-phase plutonium alloys in the temperature range of –30°C to 150°C after 10 to 100 years (for typical plutonium-239). Once void swelling begins, he estimates that the swelling rate will be approximately 1–2 percent per 10-year lifetime for plutonium-239. This value is similar to that found for other fcc metals. Compared with the range of swelling resulting from helium bubble formation, void swelling is the more important concern.

But more experiments are needed to pin down pertinent metallurgical variables. Experiments are also needed to determine whether plutonium is subject to other potential problems that arise within irradiated metals and alloys, such as irradiation-induced segregation, which can preferentially transport solute atoms into and out of local regions (impacting phase stability), and mechanical deformation. Because we are attempting to measure the effects of decades, methods must be developed to accelerate the damage process. The best method proposed to date is the doping of plutonium with small fractions of plutonium-238 (note that plutonium-238 generates almost 300 times greater α-decay activity than plutonium-239). This accelerated-aging experiment is just beginning in a joint effort between the Los Alamos and Lawrence Livermore National Laboratories.

We present these possible effects of self-irradiation as a caution. A scientific comparison with other materials subjected to external radiation fields tells us that self-irradiation of plutonium near ambient temperature has all the requisites for potentially catastrophic damage. Yet, our experience with plutonium over several decades shows no evidence for such damage. However, we know that, even if lattice defect structures induced by self-irradiation are insufficient to cause some of the catastrophic effects discussed, they may affect diffusion and transport properties, which could accelerate the kinetics of phase instability. With the new emphasis on extended lifetimes for plutonium and long-term storage, it behooves us to better understand the fundamental processes behind irradiation damage and the concurrent healing processes. ∎

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