

Plutonium metallurgy: The materials science challenges bridging condensed-matter physics and chemistry

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Abstract

Although there exists evidence of metallurgical practices dating back over 6000 years, studies of Pu and Pu alloys have been conducted for barely 60 years. During the time of the Manhattan Project and extending for some time afterward, the priority to produce the metal took precedence over the fundamental understanding of the metallurgical principals. In the past decade or so, there has been a resurgence in the basic metallurgy, condensed-matter physics, and chemistry of Pu and Pu alloys. These communities have made substantial progress, both experimentally and theoretically in many areas; however, many challenges still remain. The intent of this brief overview is to highlight a number important challenges that we face in the metallurgy of Pu including phase transformations and phase stability, aging, and the connection between electronic structure and metallurgy. © 2006 Elsevier B.V. All rights reserved.

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1. Introduction

The origins of metallurgy have been traced back to the highlands of western Asia, northwest of the Persian Gulf, as early as the year 4300 BC [1]. By 2000 BC, smelting, melting, casting, annealing, and forming of metals such as gold, silver, copper, tin, lead, and iron had been practiced. Between 2000 BC and 1800 AD, advances in metallurgy clearly impacted society in many major ways in the arts, agriculture, industry, and military applications. The Bronze Age gave way to the Iron Age and by the beginning of the 19th century, the industrial need for steel drove metallurgy to become an important discipline connecting chemistry, physics, and mechanics. Matthiessen's rule, based on an 1867 electrical conductivity investigation, is credited as the beginning of the "physics of metals", solid-state physics, and now condensed-matter physics. Phase diagram investigations, the development of the constitution of alloys, and the principles of heterogeneous equilibria by Willard Gibbs were first published in 1876. Around the same time, physical chemistry was laying the basis for the study of phase transformation kinetics. By the end of the nineteenth century, metallurgy had established

its role in the inter-space between condensed-matter physics, chemistry, and crystallography.

During the twentieth century, tremendous advances in metallurgy were made possible by von Laue's (1912) discovery of the diffraction of X-rays and the subsequent developments by Bragg and others in the studies of crystal structures. This technology opened the door to crystallographic and microstructural studies of metals and alloys and the discovery of superlattice structures, Hume-Rothery alloys, Laves compounds, and the importance of point defects. Furthermore, significant developments in the understanding of solidification, nucleation and growth theory, plasticity, texture, failure, martensitic phase transformations, diffusion, and many other physical and mechanical properties of metals and alloys were made. Scientific advances in physical metallurgy clarified our understanding that processing of metals and alloys is responsible for setting the microstructure, and that the microstructure is closely related to the performance of materials. Microstructure-properties-processing-theory relationships will undoubtedly continue to be the central component of 21st century materials science.

The understanding of metallurgy gained over the previous centuries created a fundamental base for learning and understanding how to process and characterize the new element plutonium when it was created by Seaborg, Kennedy, and Wahl in 1940 [2]. The earliest stages in Pu metallurgy were motivated

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by the need to produce a product; at that time, quantity took precedence over quality, and thus much of the basic science was left untouched. Problems with consistent density and phase transformations led C.S. Smith to suggest that intentionally alloying of Pu may be the answer and ultimately, an alloy of 3.0–3.5 atomic percent Ga was used in the Trinity test [3]. From 1945 onward, a tremendous amount of effort was placed on determining phase diagrams and phase stability of the actinide metals. Bochvar et al. [4], Ellinger et al. [5], Zachariassen and Ellinger [6], Chebotarev et al. [7], Orme et al. [8], Timofeeva [9], Hecker and Timofeeva [10] and many others contributed significantly to the understanding of the crystal structures, phase diagrams, and phase stability of Pu and its alloys.

In the last two decades, the motivation for Pu science has somewhat shifted. No longer is the sole purpose to produce a particular product. Rather, the need is to understand the fundamental underpinning of properties. In addition, the problem of aging of Pu has dictated much of the science being now developed [11,12]. The continuous radioactive decay of Pu produces an array of impurity daughter products that accumulate with age. How the damage introduced by radioactive decay and the resulting impurities affect metallurgical aspects of Pu, such as phase transformations and magnetic properties, are areas of intense research. Today, Pu science is mainly focused on the understanding of the fundamental relationships between electronic structure, crystallographic aspects, phase stability, and the roles of microstructure, impurities, and defects.

The boundaries between metallurgy, condensed-matter physics, and physical chemistry in the study of Pu are now overlapped more than ever. Recent advances in our understanding of this intriguing material are being made in all areas of physical science. This overview will highlight a number of these exciting advances and will focus on the significant challenges in the field of Pu metallurgy. Among the topics to be discussed are phase transformations and phase stability, metallurgical consequences of aging, and the important connection between electronic structure and materials physics. Substantial advances have been made in our understanding of the phase diagram, but details of the thermodynamics and kinetics of low temperature transformations, particularly below ambient, remain unclear. Advances have been made in our knowledge of the $\delta \rightarrow \alpha'$ isothermal martensitic transformation [13–16], but still much is unknown about the atomistic mechanisms and kinetics of this transformation during temperature or pressure excursions. Even after 30+ years, the origin of the double-C kinetics in the published time-temperature-transformation (TTT) diagram remains essentially unresolved. Natural aging of Pu has been the focus of significant recent efforts [17], but we still do not fully understand the basis of such features as the lattice parameter expansion with time, the volume increase which can be significantly different from that expected from the lattice parameter expansion, the vacancy migration energy, or the mechanism that appears to limit the size of the helium bubbles that form from alpha decay of Pu into U and He. The connections between the electronic structure, lattice dynamics, and microstructural details continue to present a significant challenge.

With many years of accumulated metallurgical knowledge about almost every element in the periodic table, we substantially understand most metals. Hopefully, research during the 21st century will help to eliminate many of the still perplexing details of the deeply complex structure-properties-processing relations in Pu. This is a very exciting time to be engaged in Pu metallurgy. With ever-improving computational capabilities and significant focus on electronic structure calculations and experiments, there are now collaborative worldwide efforts to advance our understanding.

2. Phase transformations and phase stability

For decades, researchers in the West followed the published Pu–Ga phase diagram developed by Ellinger et al. that indicated a region of face-centered cubic δ phase stability, extending to sub-ambient temperatures, for Ga contents between approximately 2 and 9 at.% [5]. During this same time, following the phase diagram studies by Chebotarov et al. [7], researchers in the former Soviet Union considered the possibility that the δ phase is only metastable at ambient temperatures, and, if it were not for exceedingly slow kinetics, would decompose via a eutectoid reaction to the monoclinic α phase and the compound Pu_3Ga . Although the Chebotarov et al. phase diagram showing the eutectoid [7], and the calculation by Adler in 1991 [18] of a eutectoid transformation that essentially confirmed this were available in the West, it was only after the Hecker and Timofeeva publication “A Tale of Two Diagrams” in Los Alamos Science in the year 2000 [10] that increasing worldwide consensus on the eutectoid decomposition has developed. The phase diagram calculations by Adler using the FACT program [18], by Baskes et al. using a modified embedded atom method potential within a molecular dynamics simulation [19], and by Turchi et al. using the CALPHAD program [20] have predicted the eutectoid reaction. The Third Law of Thermodynamics also dictates that a wide solubility δ phase is unlikely to be stable at temperatures near 0 K [21,22].

The thermodynamic details of the phase diagram, dictated by the free energy of the phases as a function of temperature and composition, also play a prominent role in the low temperature $\delta \rightarrow \alpha'$ transformation [22]. In the most simplistic of terms, the thermodynamics dictates the lowest energy phase, but the activation barrier between the phases along the transformation path will control the kinetics of the phase transformation.

Plutonium alloys are notoriously inhomogeneous. The sharp decline in the $\delta \rightarrow \alpha'$ transformation temperature with increasing Ga content means that an inhomogeneous alloy could transform over a wide range of temperatures that vary significantly from the martensite start temperature for the average composition. Therefore, it is important to understand how to thoroughly homogenize the material. Early studies on the homogenization of δ phase alloys demonstrated the importance of time at temperature in equilibrating the Ga concentration inhomogeneities across the grains [23]. The diffusion of Ga in ϵ -Pu is rapid, with a diffusion coefficient $D \sim 10^{-8}$ to 10^{-7} cm^2/s . This compares with the much lower diffusion coefficient of Ga in the δ -Pu, $D \sim 10^{-14}$ to 10^{-11} cm^2/s [24].

Recent studies have increased our understanding of the role of homogenization treatments on the microstructure and Ga uniformity [13,24]. These studies, which experimentally varied the homogenization time, coupled with thermodynamic modeling, indicate that full Ga homogenization is not likely to occur for anneals lasting less than 200 h, and as many as 720 h are required for full homogenization. Experimentally, Oudot used electron microprobe analysis in his Ph.D. dissertation to map the Ga segregation in non-homogenized and homogenized specimens [25]. As expected, the measured properties in homogenized and non-homogenized samples differed, sometimes significantly. The importance of these collective works is that we now have more confirmation of the importance of homogenization and also know how to retain at ambient temperatures the metastable δ -phase. However, it is also more evident that not all alloy studies reported in the literature involved fully homogenized samples.

2.1. The $\delta \rightarrow \alpha'$ isothermal martensitic transformation

Upon cooling to sub-ambient temperatures, δ partially transforms to α' (the prime denotes Ga in the alpha lattice) via a martensitic transformation mode [8,26–29]. Similarly to the δ -phase at ambient temperatures, α' is also a metastable phase. Faiers et al. [26] and Orme et al. [8], using a quench and hold technique, were the first to demonstrate that the low temperature $\delta \rightarrow \alpha'$ transformation occurs via an *isothermal* martensitic mode. The time-dependent nature of this transformation is quite different from the athermal martensites that occur in Fe–C steel, Ni–Al, Ni–Ti, and Ti–Pd alloys, among many others, in which the amount of the martensitic product is solely related to a change of temperature. The $\delta \rightarrow \alpha'$ isothermal martensitic transformation can also be induced and characterized with continuous cooling experiments using techniques such as electrical resistivity, dilatometry, and differential scanning calorimetry (DSC) [14,28,29]. Faires et al. [26], Orme et al. [8], Deloffre et al. [30], Hecker et al. [28], and others have shown that martensite start (M_s) temperature is a function of the Ga content. Adler and Olson have shown also that the M_s temperature is a function of grain size; the larger the grain size, the higher the M_s temperature [31]. Blobaum et al. have recently shown that the $\alpha' \rightarrow \delta$ reversion occurs via a burst martensitic mode and hence they use M_B as a symbol for M_s [14]. In their work concerning the $\alpha' \rightarrow \delta$ reversion, DSC experiments show periodic spikes in the heat flow, indicating that the transformation occurs in well-separated packets of temperature, while dilatometry and resistometry traces through the reversion exhibit steps, again indicating a burst mode. The derivatives (the change in length with a change in time (dL/dt) and change in resistivity with change in time ($d\Omega/dt$)) reveal periodic spikes. The periodicity of the bursts is quite similar among the different techniques and among the different samples. The authors point out that the $\delta \rightarrow \alpha'$ forward transformation on cooling requires the nucleation of α' particles, whereas no nucleation is most likely needed in the $\alpha' \rightarrow \delta$ reverse transformation.

During continuous cooling experiments, the amount of $\delta \rightarrow \alpha'$ transformation in Pu–1.8 and 2.0 at.% Ga alloys decreases with each thermal cycle as shown by Hecker et al. [28] and

Mitchell et al. [24] even though it appears that all α' reverts to δ during the cycle. In very recent work, Blobaum et al. have shown that the amount of the $\delta \rightarrow \alpha'$ transformation is dependent on details of the thermal cycling [32]. In these experiments, it was shown that, after a cooling and heating cycle, or after a high temperature anneal (375 °C), in order to fully reproduce the same amount of transformation on subsequent cooling, the sample must be “conditioned”, or annealed at room temperature for a minimum of 6 h. Conditioning times shorter than 6 h produce correspondingly smaller amounts of transformation on subsequent coolings to the transformation temperature range. Other conditioning temperatures were examined in that study, and conditioning at room temperature was found to result in the largest amount of transformation. The authors proposed that α_m embryos might be forming as a precursor to the $\delta \rightarrow \alpha + \text{Pu}_3\text{Ga}$ eutectoid reaction. These α_m embryos, postulated to have the same composition as the δ matrix, initiate or trigger α' on subsequent cooling. Appreciating that some processes occur at room temperature is important in experimental metallurgy of Pu, as these works nearly always involves some holding at ambient conditions.

Transmission electron microscopy (TEM) and diffraction investigations by Zocco et al. [27] have provided extensive insight into the crystallography and morphology of the $\delta \rightarrow \alpha'$ transformation. The orientation relationship between the α' particles and the δ matrix was determined to be $(1\ 1\ 1)_\delta \parallel (0\ 2\ 0)_{\alpha'}$ and $[-1\ 1\ 0]_\delta \parallel [1\ 0\ 0]_{\alpha'}$. The authors also showed $(2\ 0\ 5)_{\alpha'}$ twinning as a lattice invariant deformation mode. Moore et al. applied dark-field TEM to the partially transformed two-phase structure and showed that the α' particles consist of two variants rotated 60° around the $(0\ 2\ 0)_{\alpha'}$ direction [16]. High resolution TEM revealed that the α'/δ interface is composed of a terrace and ledge structure that is faceted on $\{1\ 1\ 1\}_\delta$, in line with the topological model discussed by Hirth et al. [15]. A number of studies, beginning with Choudhry and Crocker [33], then Olson and Adler [34], and Jin et al. [35] applied theories of martensite crystallography to determine the habit plane of the α' particles in the δ matrix. Most of these studies predicted a $\{1\ 2\ 3\}_\delta$ habit plane with 24 variants, whereas optical metallography revealed only 4 variants, possibly implying a $\{1\ 1\ 1\}_\delta$ habit plane. Looking forward, additional TEM experiments, including *in situ* heating and cooling experiments will undoubtedly provide important insights into the transformation crystallography, habit plane, and mechanism.

2.2. Double-C curve kinetics

One of the longest standing mysteries in the metallurgy of Pu involves the kinetics of the $\delta \rightarrow \alpha'$ isothermal martensitic transformation as depicted in the experimentally determined time-temperature-transformation (TTT) plots [26,8]. The TTT diagrams of Pu–0.6 at.% Ga and Pu–0.7 at.% Ga alloys reveal only one C curve, whereas the Pu–1.4 and 1.9 at.% Ga alloys show that there are two separate knees at ~ -130 °C and ~ -155 °C. Orme et al. suggested that the transformation in the upper C was a result of a massive transformation while the lower C was a result of a martensitic transformation [8]. Deloffre reported diffusive

and displacive components of the transformation and suggested a change in the mechanism that occurs at ~ 1.5 at.% Ga [30]. The occurrence of the double C implies the possibility of two distinct, thermally activated mechanisms existing for this transformation. Recent DSC work by Oudot et al. adds supporting evidence for the double-C behavior and reveals an interesting precursor phenomenon [36]. DSC scans on cooling to a sub-ambient isothermal hold temperature reveal three peaks; the first begins at approximately -103 °C, the second begins at approximately -117 °C, and the third begins at approximately -131 °C. A plot of the area of the reversion peak (i.e., the amount of $\delta \rightarrow \alpha'$ reversion) versus isothermal holding temperature reveals two maxima after 18-h holds at -130 °C and -155 °C.

Although these experiments are shedding further light on the kinetics of the transformation, we still do not understand the basic reason for the double-C plots. Do they result from different transformation mechanisms, different transformation paths, different morphologies, different embryos or nucleation sites, or something else?

2.3. The pressure-induced $\delta \rightarrow \alpha'$ transformation

The $\delta \rightarrow \alpha'$ transformation can also be induced by the application of pressure. Under pressure, the $\delta \rightarrow \alpha'$ transformation and reversion characteristics are a strong function of the particular alloying element and its content. A Pu–2 at.% Al alloy is reported to transform first to β' then to α' under isostatic pressure [37]. Pu–Ga alloys, however, transform directly to α' and undergo either a direct ($\alpha' \rightarrow \delta$) or indirect ($\delta \rightarrow \beta' \rightarrow \gamma' \rightarrow \alpha'$) reversion depending on Ga concentration [28]. Reversion characteristics are remarkably similar to those in the low temperature $\delta \rightarrow \alpha'$ transformations. Why do Pu–Al alloys transform through β' whereas Pu–Ga alloys transform directly to α' ? Or do they? Recently, diamond anvil cell experiments by Faure et al. on a Pu–2 at.% Ga alloy reveal a $\delta \rightarrow \gamma' \rightarrow \alpha'$ transformation sequence [38]. In addition, these authors performed time-dependent experiments by pressurizing a specimen to 1.76 GPa and measuring the unit cell volume as a function of time. The volume was observed to decrease over a period of approximately 300 days before reaching a saturation value. This saturation value is close to that obtained by a slow addition of pressure of 0.1 GPa per day. Both of these atomic volumes are greater than that of unalloyed Pu for the same pressure level.

Hecker et al. described an experiment in which the lattice parameters of the α' unit cell were measured with X-ray diffraction shortly after a pressure-induced transformation and then approximately 1 year later [28]. They observed a decrease in the α' unit cell volume over that period and suggested that Ga may be migrating to one of eight unique lattice sites within this monoclinic unit cell. Sadigh and Wolfer performed density functional theory (DFT) calculations in which the molar volume of a Ga atom was determined for each of the eight unique sites of the α' unit cell [39]. The results indicate that indeed the lowest energy configuration for a Ga atom in an α' unit cell is when the atom is located on site 8. Does the time dependence of the α' volume change suggest Ga hopping to site 8? Experimental determination of the Ga occupation on site 8 using techniques

such as extended X-ray absorption fine structure (EXAFS) may shed some light on these calculations.

2.4. Significant issues involved in the $\delta \rightarrow \alpha'$ transformation

In recent years, we have obtained a reasonable understanding of the eutectoid transformation, the metastability of the δ phase, the crystallography of the α' phase, and the importance of a conditioning treatment. We have been reminded of the importance of solute homogenization and in turn, become aware that not all samples reported in the literature have been fully homogenized. However, we have work to do to better understand the fundamental science underlying the double-C plots, the mechanism or mechanisms of the $\delta \rightarrow \alpha'$ transformation and its kinetics, the reason for the precursor phenomenon observed in DSC, the $\delta \rightarrow \alpha'$ transformation under pressure, and the role of site 8 in the α' structure.

3. Aging

Over the past 6 or so years, the evaluation of aging phenomena in Pu alloys has received increased attention [11,12,39–48]. The self-irradiation caused by the decaying Pu isotopes lies at the nexus of the age-related microstructural changes. The principal radioactive decay mechanism of Pu is that of alpha decay, which transmutes the Pu atom into a U atom and an alpha particle occurs at a rate of approximately 41 appm/year (atomic parts per million per year). The 86 keV ^{235}U recoil traverses the lattice approximately 12 nm and in doing so, creates on the order of 2300 Frenkel pairs. The vast majority of these defects return to δ phase lattice sites, but a small fraction, approximately 10% may remain in form of free interstitials and vacancies or interstitial or vacancy clusters [41,42]. Research emanating from the nuclear reactor community has demonstrated that these microstructural processes ultimately result in property changes that include void swelling, hardening, and reduction in ductility.

Opposite to the ^{235}U recoil, a 5 MeV alpha particle traverses the lattice approximately 10 μm , losing its energy via electronic excitations before coming to rest with the generation of an additional 265 Frenkel pairs. Two electrons join the alpha particle to become a He atom, leading to a helium generation rate of approximately 41 appm/year. Positron annihilation data by Howell et al. [49] indicate that the He atom immediately finds an unfilled vacancy. Three principal aging mechanisms have been identified as a result of the self-irradiation of Pu isotopes that would cause dimensional changes: the initial transient, helium accumulation, and void swelling. The initial transient is an effect that results in a lattice parameter increase [50,25]. The second contributor to dimensional change is the build-up of helium as a result of the alpha decay [43]. The third possible age-related phenomenon is void swelling [51], but this has not yet been observed in naturally aged Pu alloys [43] nor been predicted by theory [39].

3.1. Lattice parameter swelling and volumetric swelling

When Pu is alloyed with Ga, the lattice parameter of the fcc δ phase decreases with increasing Ga content [5]. However,

two reports suggest that the lattice parameter of Pu–Ga alloys increases substantially with time at ambient temperature during the early stages of aging [50,25]. Much of the initial increase is observed to occur during the first 3 months. After approximately 1 year, no more lattice parameter expansion is observed in contrast to dilatometry results measuring length changes of Chung et al. [48], which show the initial volumetric increase is followed by an extended linear region with a small positive slope. In comparing the volume expansion due to lattice parameter increases with time as measured by X-ray diffraction, with the macroscopic volume expansion as measured with dilatometry, which should include both the expansion due to the lattice parameter increase and the extra volume created by the presence of He bubbles [43], it was found that the macroscopic volume change is significantly smaller than the cumulative change expected from the above two effects. A hypothesis to explain this counter-intuitive behavior has been proposed by Wolfer et al. [45]. They suggest that small precipitates of the higher density ζ -Pu₃Ga phase form in the δ matrix as a first stage in the eutectoid decomposition. In doing so, approximately 10% of the available Ga in the δ phase is removed from the matrix, thus increasing the lattice parameter of the δ phase. Radiation-induced disordering (dissolution) of the ζ -Pu₃Ga phase reaches a steady state leading to the termination of the lattice parameter expansion. So far, this is the only hypothesis to explain the interesting relationship between volume expansion and lattice parameter expansion. Additional experiments focused on the composition of the matrix and existence of the ζ -Pu₃Ga phase, coupled with first-principles and CALPHAD calculations, are needed.

Applying electrical resistivity experiments, Lee et al. [52], Elliott et al. [53], and Wigley [54] studied the radiation damage annealing characteristics and reported the isochronal annealing curves of alpha, delta (Pu–Al samples) and deformed alpha samples. Fluss et al. have published isochronal annealing data for a Pu–3.3 at.% Ga alloy that reveal the five stages of annealing [17]. These isochronal annealing experiments indicate that stage V, the temperature at which vacancy clusters are mobile, is slightly above room temperature. This suggests most of the radiation damage should be annealed out at room temperature. Annealing slightly above room temperature should remove all of the accumulated radiation damage. However, dilatometry experiments by Kozlov et al. on Pu alloys aged naturally [55], and Freibert et al. on an alloy isotopically conditioned for accelerated aging [56] at the equivalent of 48 years of natural aging exhibit a volume contraction at $\sim 150^\circ\text{C}$. Electrical resistivity experiments on aged materials also reveal a large change in the vicinity of 170°C [46]. If the radiation damage already anneals out slightly above room temperature, what is the origin of this volume reduction during heating near $\sim 150^\circ\text{C}$? Could this volume contraction be the proposed ζ -Pu₃Ga phase dissolving back into solution?

The questions here open the various possibilities of property changes related to the onset of the early stages of the eutectoid reaction, $\delta \rightarrow \alpha + \text{Pu}_3\text{Ga}$, which have hitherto not been considered important in the literature because of the implied long term sluggishness of his reaction ($\sim 10,000$ years). The just published

“ δ conditioning” experiments at 25°C [32] mentioned in Section 2.1 and the volume changes and electrical resistivity changes at $150\text{--}170^\circ\text{C}$ suggest that the eutectoid reaction may be at least a partial reason for these changes, and hence that a pursuit of a much better understood explanation of these changes is justified.

3.2. Helium bubbles

Transmission electron microscopy reveals tiny He bubbles by the Fresnel Fringe Technique in naturally and accelerated aged materials [43]. In total, over 40,000 bubbles have been characterized in many different samples. The average size was determined to be ~ 1.4 nm with a number density on the order of $(1\text{--}2) \times 10^{17} \text{ cm}^{-3}$ for samples between 16 and 44 years old. Rate-equation modeling has been performed to predict the change in concentration of He in solution as a function of time, the size of the He bubbles as a function of time, and the number density as a function of time [43]. In the generation of the model, the following assumptions were made: (1) the He atom immediately finds a vacancy; (2) the He-filled vacancy diffuses through the lattice; (3) when two He-filled vacancies meet, they form a stable dimer; (4) there is no thermally activated removal of He from the bubble, i.e., there is no amount of thermal activation that would eject a He atom from a bubble. The experimental results indicate that the He bubble size appears to increase in the early years of aging then remain constant at ~ 1.4 nm while the number density continues to increase. The unresolved question is, why does the He bubble size appear to saturate at ~ 1.4 nm? We have indications from positron annihilation that the bubbles that form in the first few months have a low helium to vacancy (He/V) ratio. This He/V ratio is observed to increase with time and it is believed to reach a level of approximately 2.5. At this point, it is conjectured that the pressure inside the bubble and its associated strain field become repulsive to incoming He-filled vacancies. This size-limiting mechanism would then lead to a constant bubble size and a concurrent increase in the number density.

3.3. Significant issues in aging

Over the past few years, the improved MEAM potential within molecular dynamics simulations has been applied to study the cascade damage and properties of He bubbles. Density functional theory has been applied to evaluate the effects of actinide daughter products on the stability and lattice parameter of aging Pu alloys and to the propensity for void swelling. Transmission electron microscopy has revealed the presence of nanometer He bubbles with an average size of ~ 1.4 nm and a number density on the order of $(1\text{--}2) \times 10^{17} \text{ cm}^{-3}$. There remain, however, a number of outstanding questions regarding the fundamental aging process. We still have work to do to better understand the fundamentals of the lattice parameter and volume expansion in the early stages of aging, the volume change upon heating to $\sim 150^\circ\text{C}$, and the He bubble size limit at ~ 1.4 nm.

4. The relation between electronic structure and metallurgy

Theoretical predictions of the stability of phases have been performed using density functional theory (DFT) [57] and using molecular dynamics with a modified embedded atom method (MEAM) potential [19]. These calculations are able to predict the relative stability of the many phases of unalloyed Pu and to predict the volumes of the allotropic phases. Although there remains some controversy about the method itself and the assumptions, DFT has provided significant insight into the nature of Pu and Pu alloys. What the first principles methods provide are the relative ground state energies, bulk modulus and volumes of the phases. What they are less likely to provide is insight into the kinetics of the phase transformations and the response of the material to strain-inducing defects. A look into the correlation between the electronic structure and metallurgy lies in the elastic anisotropy and the phonon dispersion curves. Ledbetter and Moment [58], using the ultrasonic technique, were first to show that δ -phase Pu alloys are the most elastically anisotropic fcc materials known. The anisotropy ratio of ~ 7 was confirmed with high-resolution inelastic X-ray scattering measurements of the phonon dispersion curve [59,60]. Recently, Moore et al. calculated bond strengths between neighboring atoms in unalloyed and alloyed δ -phase Pu using DFT [61]. For the unalloyed Pu fcc δ structure, the calculations indicate that the bond strengths between near neighbor atoms are significantly asymmetric and suggest that any perturbation (defect causing local strain) to the lattice will result in a non-linear response. Alloying with Ga significantly reduces the bond strength anisotropy, but in small microstructural regions depleted of Ga, one would expect anisotropic distortions closer to those in pure δ Pu. This work provides an interesting insight into the possible behavior of the δ alloys at low temperatures, or increasing pressure, or during aging. In the case of low temperature excursions, once T_0 (the temperature at which the free energies of the δ and α' are equal) is reached on cooling, the α' phase becomes the lowest energy phase and δ should begin to transform to this structure. However, an activation barrier, dictated by strain energy and surface energy resists the transformation. If embryos, or nuclei of the α' phase begin to form, the δ matrix will accommodate this transformation with a minimum increase of energy. Anisotropic elastic strains, dictated largely by the anisotropic nature of the bonds will accommodate some of the perturbations. Lawson et al. have observed these microstrains in a specimen cooled to low temperatures [62]. For larger volume changes, plastic deformation in the matrix will occur.

A similar connection between electronic structure and metallurgy can likely be found in the case of the He bubbles. As described earlier, the size of the bubbles appears to reach a near-constant value, while the number density continues to increase. It is conjectured that this results from an increase in the pressure within each bubble that ultimately makes it unfavorable for additional He-filled vacancies to enter. It may be that the anisotropic bonding coupled to the lattice strains resulting from the pressure inside the He bubble resist additional He atoms from entering the bubble.

The phonon dispersion curves of δ -phase Pu–Ga alloys, γ -Ce, Th, La and other f-electron materials exhibit a pronounced softening in the transverse $\langle 111 \rangle$ branch [59,60,63–65]. Stassis et al. suggest that this could be a precursor of the fcc–dhcp structural phase transition in Ce. However, recent work by Farber has shown that the $\langle 111 \rangle$ transverse mode softening also occurs in the α -Ce phase [66]. This means that the large softening of the transverse $\langle 111 \rangle$ branch may be something that is intrinsic to materials with occupied or unoccupied f states. More experimental and theoretical work is needed to understand the relation of the phonons to the microstructural response.

5. Summary

Researchers around the world have made great strides in recent years in our understanding of the many metallurgical and electronic structure features of Pu and Pu alloys. Our better understanding of problems resulting from inhomogeneous samples, phase diagram details, and phonon dispersion curves are but a few examples. Excellent progress has also been made in the areas of conditioning (annealing) times required for reproducible amounts of low temperature transformation, the burst nature of the reverse martensitic transformation, and the fundamental aspects of Pu aging. However, there remain many significant questions that we are now in a position to address with additional experiments and theory. These include:

- (1) The explanation of the observed double-C curve kinetics, including the mechanism(s) of transformation, nucleation features, and the interesting precursor phenomenon.
- (2) The $\delta \rightarrow \alpha'$ transformation under pressure and the formation of an intermediate β' phase in Pu–Al alloys, and the γ' phase in Pu–Ga alloys.
- (3) The lattice parameter and volume changes with time occurring in Pu–Ga samples and their relation to the early stages of aging. The large volume decrease that occurs at $\sim 150^\circ\text{C}$.
- (4) Helium bubble size reaching a limit at ~ 1.4 nm.
- (5) The effect of the electronic structure on the metallurgy of δ Pu alloys at near atomistic dimensions and the role of phonons in determining the response of the material to defects.

Addressing these questions will take us a long way toward a deeper understanding of the metallurgy of plutonium. The answers lie in the materials science embedded between the condensed-matter physics and chemistry.

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