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Computer-aided materials research is now an integral part of science and technology. It becomes particularly valuable when comprehensive experimental investigations and materials testing are too costly, hazardous, or of excessive duration; then, theoretical and computational studies can supplement and enhance the information gained from limited experimental data. Such is the case for improving our fundamental understanding of the properties of aging plutonium in the nuclear weapons stockpile.

The question of the effects of plutonium aging on the safety, security, and reliability of the nuclear weapons stockpile emerged after the United States closed its plutonium manufacturing facility in 1989 and decided to suspend any further underground testing of nuclear weapons in 1992. To address this, the Department of Energy's National Nuclear Security Administration (NNSA) initiated a research program to investigate plutonium aging, *i.e.*, the changes with time of properties of Pu-Ga alloys employed in the nuclear weapons and to develop models describing these changes sufficiently reliable to forecast them for several decades [1]. The November 26, 2006 press release by the NNSA summarizes the conclusions of the investigation, "… there appear to be no serious or sudden changes occurring, or expected to occur, in plutonium that would affect performance of pits beyond the well-understood, gradual degradation of plutonium materials." Furthermore, "These studies show that the degradation of plutonium in our nuclear weapons will not affect warhead reliability for decades," then NNSA Administrator Linton Brooks said. "It is now clear that although plutonium aging contributes, other factors control the overall life expectancy of nuclear weapons systems [2]."

The origin of plutonium aging is the natural decay of certain plutonium isotopes. Specifically, it is the process of alpha decay in which a plutonium atom spontaneously splits into a 5 MeV alpha particle and an 85keV uranium recoil. The alpha particle traverses the lattice, slowly loosing energy through electronic excitations, acquiring two electrons to become a helium atom, then finally coming to rest approximately 10 microns away with the generation of a few-hundred Frenkel pairs. The uranium recoil immediately displaces a couple-thousand Pu atoms from their original lattice sites. This process, which occurs at a rate of approximately 41 parts-per-million per year, is the source of potential property changes in aging plutonium [3].

Plutonium aging encompasses many areas of research: radiation damage and radiation effects, diffusion of point defects, impurities and alloying elements, solid state phase transformations, dislocation dynamics and mechanical properties, equations of state under extreme pressures, as well as surface oxidation and corrosion. Theory, modeling, and computer simulations are involved to various degrees in many of these areas.

The joint research program carried out at Lawrence Livermore National Laboratory and Los Alamos National Laboratory encompassed experimental measurements of numerous properties of newly fabricated reference alloys, archival material that have accumulated the effects of several decades of radioactive decay, and accelerated aging alloys in which the isotropic composition was adjusted to increase the rate of self-irradiation damage. In particular, the physical and chemical processes of nuclear materials degradation were to be studied individually and in great depth. Closely coupled to the experimental efforts are theory, modeling, and simulations. These efforts, validated by the experiments, aim to develop predictive models to evaluate the effects of age on the properties of plutonium.

The need to obtain a scientific understanding of plutonium aging has revitalized fundamental research on actinides and plutonium in particular. For example, the experimental discovery of superconductivity in Pu-based compounds [4], the observation of helium bubbles in naturally aged material [5], and the measurement of phonon dispersion properties in gallium-stabilized delta plutonium [6-8] have occurred in recent years. On the theory frontier, dynamic mean field theory calculated the phonon dispersion curves [9] before the measurements were published and the application of spin-polarized density functional theory has resulted in reproducing the energies and densities of the light actinides [10] and all plutonium phases in remarkable agreement with observed results [11, 12]. The delta, or face-centered-cubic phase, in particular, has been shown to have an anti-ferromagnetic spin configuration. Because this is in apparent contradiction to experiments [13] that reveal no evidence of anti-ferromagnetic behavior, a lively scientific exchange of ideas and opinions among actinide researchers has taken place, and electronic structure theory and experiments for actinides has become exciting fields of research [14-19]. Needless to say, it is not possible to cover all activities in this particular issue, and so, only a limited number of vignettes from some areas are presented. The papers and their relationships to plutonium science and aging are as follows.

The paper by Yang *et al*. describes some very large scale, *ab initio* electronic structure calculations of actinide metals, particularly uranium and plutonium. The authors review the challenges specific to high-Z metals and describe their approach using an efficient massively parallel planewave implementation on large supercomputers, including BlueGene/L at Lawrence Livermore National Laboratory. The authors first discuss the pair-correlation function of uranium, and then describe their efforts to evaluate the properties of plutonium as a function of age. The radioactive decay of a plutonium atom introduces a uranium daughter product and a helium atom. In order to quantify the change in the compressibility of plutonium with age, calculations are presented for the α-phase of plutonium with a U atom replacing a Pu atom and with helium in an interstitial position located farthest from the U atom. The calculations indicate that upon relaxation, the interstitial He atom displaces neighboring Pu atoms outward. Here, it was determined that the effects of aging, i.e., the ingrowth of U and He have a negligible effect on the compressibility of Pu relative to other factors. In studying a Pu-Ga alloy, these authors substituted a Ga atom at the most open lattice site in the α-phase structure as well as the most closed site. In both cases, the calculations indicated that neighboring Pu atoms are displaced outward from the Ga atom.

The next paper by Söderlind *et al*. is another first-principles investigation of density changes in monoclinic α-Pu when a Pu atom is replaced by an atom of Al, or Ga, or Am. The application of the exact muffin-tin orbital method incorporated with the coherent potential approximation and an all-electron full-potential linear muffin-tin orbital method both predict different density changes depending on which lattice site is occupied by the substitutional atom. Similar to the results of Yang *et al*., these calculations predict a lattice expansion when Ga or Al atoms are substituted on site #1. When the substitution is made in site #8 of the unit cell of α-Pu, only a small volume expansion occurs.

First-principles calculations for actinide metals are invaluable for determining the ground state crystal structures and the energies and volumes of alternative phases. However, these calculations are still restricted to computational cells containing a few hundred atoms. To study larger systems, empirical interatomic potentials must be employed. Valone and Baskes describe their continued development of such a potential with the Modified Embedded Atom Method (MEAM), and apply it in Molecular Dynamics (MD) simulations of collision cascades in Pu. The simulations probe the number of atoms displaced by a 20 keV recoil along the <124> direction of the face-centered cubic δ-phase lattice from the beginning of the collision stage up to 250 fs.

Kubota *et al*. greatly extend the simulation time in a collision cascade, in some cases up to 2 ns, and the energy range between 20 KeV and 85 keV in order to explore all three stages: the collision stage, the thermal spike stage, and the annealing stage. The latter provides the final result needed as input to models and codes that follow the long-term evolution of the microstructure over periods of years and decades, such as the nucleation and growth of dislocation loops, of voids, and of helium bubbles. Kubota *et al*. discover that the annealing stage in δ-Pu is exceedingly long in comparison to other metals with the face-centered-cubic structure.

In another application of the MEAM potentials, Baskes *et al*. explore short-range ordering of Ga in δ-Pu alloyed with 5 at.% Ga, employing both MD and Monte Carlo simulations. The simulations are performed at 200, 400, and 600K and in each case predict that all Ga-Ga first nearest neighbor atoms and Ga-Ga fourth nearest neighbor atoms disappear and that Ga-Ga second and third nearest neighbors are favored.

Like most metals used in technological applications, Pu is also alloyed with other elements. Here, just a few atomic percent of Ga can retain the alloy in the face-centered-cubic structure, the δ-phase, which is ductile and hence malleable, unlike the very brittle monoclinic α-phase that would otherwise form. The solidification process begins by the formation of the body centered cubic ε-phase. In this phase, the diffusion of Ga is quite rapid. Upon further cooling the alloy enters the two-phase ε + δ region. Diffusion of Ga in the δ-phase is between 3 and 7 orders-of-magnitude lower than in the ε-phase. The first δ-phase to form is enriched in Ga and as the alloy further cools, Ga lean regions remain at the grain boundaries. This highly cored microstructure would lead to dramatic variations in physical and mechanical properties as well as an enhanced susceptibility to phase transformations upon further cooling. To study this coring structure evolution, Hu

et al. employ the phase-field method. They determine the δ-phase particle size as a function of annealing time, as well as the coring factor as a function of cooling rate.

The next two papers deal with radiation-induced void swelling, a general phenomenon that occurs in most metals and alloys exposed to radiation that creates displacements. There are two general conditions that must be met for void swelling: the temperature during irradiation must be sufficiently high for vacancy migration to take place, but lower than required for self-diffusion. The other condition is that there must be a positive "net bias". This net bias is a composite quantity, involving characteristic bias factors for the different sinks at which the self-interstitials and vacancies, generated by the displacement damage, are annihilated. These bias factors are essential parameters needed for radiation damage models and computer codes. Wolfer provides a review how the bias factors for dislocations are computed, and Surh and Wolfer show how bias factors for voids and bubbles are obtained.

Ductile rupture of materials deformed under high strain rates occurs by void formation, growth, and finally by coalescence of voids. Using large-scale MD simulations and EAM potentials for Cu, Rudd *et al*. study the void processes involved in ductile failure at the atomic level and compare their results with those from continuum models. Specifically, they simulated the emission of dislocations and dislocation loops from a single void, the stress-strain response during void growth in single crystals, and the coalescence of two voids as a function of the initial inter-void spacing.

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