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Equilibrium thermodynamics of radiation defect clusters in δ-phase Pu–Ga alloys

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ABSTRACT

The paper presents a theoretical investigation into the response of δ-phase Pu–Ga alloys to self-irradiation. Using classical molecular dynamics we investigate the long-term behavior of primary radiation defects (vacancies) in the face-centered cubic lattice of the alloys under ambient conditions. High diffusive migration energy barriers and the corresponding low mobility of vacancies do not allow us to track their dynamics in the lattice by direct molecular dynamics simulations. Instead, we use the Helmholtz free energy to investigate the equilibrium thermodynamics of metastable microconfigurations of Pu–Ga crystals with artificially introduced vacancy clusters in various regular and random configurations. The Helmholtz free energy of the microconfigurations are calculated with the thermodynamic integration method. Based on the free energy evaluation we draw conclusions about the relative thermodynamic stability of various microconfigurations under ambient conditions. The equilibrium parameters of vacancy clusters in the bulk of the lattice and in the presence of edge dislocations are estimated.

1. Introduction

The degradation of structural and radioactive materials properties caused by an irradiation and/or self-irradiation known as radioactive aging is the subject of great importance for nuclear applications. The self-irradiation of actinides and their alloys and compounds results in continuous production of radiogenic helium and primary radiation defects (PRDs) of crystal structure, their accumulation, diffusive migration in the lattice, clustering, *etc*. The morphology of the point defect clusters (*i.e*. equilibrium size and shape, the fraction of free and clustered defects) and interaction of the defect clusters with preexisting defects are the subjects of great importance, since they have a direct impact on properties of the materials such as elastic–plastic properties, static and dynamic strength, transport coefficients, phase stability *etc*. [1–11].

In this paper we investigate the behavior of PRDs in the form of vacancies produced as a result of collision cascade damage of the crystal structure caused by α-decays of ^{239}Pu nuclei in the bulk of the face-centered cubic (fcc) lattice of δ-phase Pu–Ga alloys. Using classical molecular dynamics (CMD) we study the long-term behavior of the PRDs in the lattice, their clusterization, possible formation of cavities, and interaction of PRD clusters with preexisting extended defects (edge dislocations).

A number of CMD and Monte Carlo simulations of the initial stage of the δ-phase Pu–Ga alloys self-irradiation (specifically lattice-damage cascades) were performed [3,12–15] with the Modified Embedded Atom Model (MEAM) [16–18] as the interatomic interaction potential. Presently there is a variety of the MEAM potential parameterizations for the elemental plutonium and binary fcc Pu–Ga alloys [10,19–21], and for the CMD simulations of the collision cascades different authors used different MEAM potential parameterizations. In spite of the differences in the details of the CMD simulations of the self-irradiation the general results obtained by different authors [3,12–14] are essentially the same:

1) The ^{235}U nuclei with the kinetic energy ~86 *keV* cause localized (5–8 *nm* in size, ~2500 Frenkel pairs) collision displacement cascades before they lose their kinetic energy. The first stage of the collision cascade formation lasts for ~0.5 *ps*.
2) The energy stored in the collision cascade causes local melting of the crystal and formation of an amorphous region. The maximal size of the melted region depends on the initial temperature, is

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about 8–10 *nm* (16,000–20,000 atoms), and is reached 10–15 *ps* after the α-decay event.

3) The next stage is a thermalization of the cascade region with the rest of the lattice and further recrystallization when the crystalline structure of the damaged region almost completely recovers in nanosecond timescale. The residual defects are 200–250 single vacancies and interstitial atoms. The interstitial atoms due to their high diffusive mobility [22,23] leave the cascade region rapidly through chains of substitutions. As a result of the fast stage (a couple of nanoseconds) of the annealing a localized depletion region of 8–10 *nm* in size with 200–250 single vacancies is formed in the vicinity of the α-decay event.
4) It is not surprising that the annealing time depends strongly on temperature. For example, at temperature $T = 600$ *K* the annealing of the melted region takes 1–2 *ns*, while if we decrease the temperature to $T = 300$ *K*, it would take five times longer [12]. Since interstitial atoms have the lowest activation energy $W = 0.084$ *eV* [22] ($W = 0.056$ *eV* [24], $W = 0.079$ *eV* [25]) among all the point defects in δ-phase Pu–Ga alloys, the annealing time is determined by the diffusive mobility of interstitial atoms which decreases by a factor of five for this decrease of the temperature. The change of the annealing times from one to tens of nanoseconds is not crucial from the viewpoint of the long-term behavior of the material. For that times the damage cascades remain isolated, do not overlap, and do not interact with each other. The general result obtained so far is the quantitative estimate of the source of primary radiation defects as 200–250 vacancies localized in the region ~10 *nm* and highly mobile interstitial atoms uniformly spread in the lattice.

The other particles produced in α-decays are α-particles with energy ~5 *MeV*. They travel much further away from the α-decay site, produce about 200 additional Frenkel pairs each, lose most of their kinetic energy trough electronic excitations, capture two electrons from the metal lattice, and become neutral He atoms, which occupy the nearest vacancies in the lattice or create and occupy vacant sites by knocking out Pu or Ga lattice atoms generating interstitial atoms [23,26–28]. Diffusive migration of secluded He atoms in the lattice occurs as a motion of He atom-vacancy complex with a diffusive activation energy ~0.7 *eV* [27] which is rather high compared to the ambient temperature thermal energy. If two diffusing He atom-vacancy complexes meet, then a nucleus of He gas bubble is formed. The questions of the solubility of helium in the fcc lattice of Pu–Ga alloys, and the mechanisms determining the equilibrium parameters of He bubbles in Pu–Ga alloys were addressed in Ref. [29] while in the present paper we investigate the behavior of compact vacancy clusters in the bulk of the fcc lattice of Pu–Ga alloys, their thermodynamically equilibrium parameters, the interaction of the vacancy clusters with preexisting extended defects, namely, edge dislocations.

While the diffusive dynamics of interstitial atoms in the fcc lattice of Pu–Ga alloys due to their high mobility is accessible for direct CMD modeling even at temperatures below ambient, the characteristic times of diffusive migration of single vacancies and vacancy complexes under ambient conditions are in the range from seconds to hours [22,30]. This makes it impossible to model their diffusive dynamics in the lattice even using accelerated CMD as was done for copper [31] with the parallel replica dynamics technique [32]. Instead, in the present study we investigate the relative thermodynamic stability of metastable microconfigurations of an ideal crystal with artificially introduced systems of defects of various morphologies using the Helmholtz free energy.

2. Details of CMD simulations

For the investigation into the relative thermodynamic stability of finite temperature systems it is insufficient to calculate and compare only the internal energies of different states. At finite temperatures the entropy contribution to the Helmholtz free energy plays an important role. If one can calculate the "absolute" values of the free energy for various metastable states of a system for the same external conditions, he/she can draw unambiguous conclusions about the relative thermodynamic stability of those states. Unfortunately the absolute values of the free energy cannot be calculated directly in CMD simulations as an average of some quantity or expressed as a function of some averages. However, it is possible to evaluate the free energy values within CMD using the so-called thermodynamic integration method (TIM) by Frenkel and Laad [33–35]. A detailed description of the proposed approach for the investigation of the relative thermodynamic stability of various metastable configurations and all the formalism for the free energy calculations used can be found in Ref. [29] where the TIM was used to study equilibrium thermodynamics of helium in δ-phase Pu–Ga alloys. The TIM proved to be an effective instrument for calculating the Helmholtz free energy, whose accuracy and thermodynamic consistency were demonstrated with numerous examples. Here we applied the TIM for the investigation into the equilibrium thermodynamics of PRDs in the binary Pu–Ga alloys. All the following simulations were performed with the widely-used MEAM [16–18] potential for interatomic interaction with the parameterization from Ref. [10] using a CMD code MOLOCH [36] developed at VNIITF.

All calculations of the thermodynamic potentials were made for δ-phase Pu-3 *at.*% Ga alloy under ambient conditions ($T = 300$ *K* and $P = 0$). Sizes of Pu–Ga alloy samples were in the range from Ref. 4,000 up to ~5 million atoms containing 3% Ga atoms as disordered substitutional solid solution with periodic boundary conditions in the cartesian directions with artificially introduced systems of defects of various morphologies.

3. Isolated primary radiation defects

As the first step we calculated the absolute values of changes in internal energy and Helmholtz free energy when a Frenkel pair (vacancy + interstitial atom) is formed. To this end we generated and well relaxed at ambient conditions twenty fcc Pu-3 *at.*% Ga samples of $10 \times 10 \times 10$ unit cells varying random positions of substitutional Ga atoms. For these samples we independently calculated and averaged internal and free energies $E_0 = -3.79$ *eV*/*atom* and $F_0 = -3.94$ *eV*/*atom*, respectively. Then we randomly chose one atom in each of the samples and replaced it by a vacancy, while the atom was put into a random interstitial site at a distance no shorter than the lattice constant $a \approx 0.462$ *nm* from the vacancy. There were no correlations between the positions of the vacancies, interstitial atoms, and substitutional Ga atoms. The total number of atoms in the sample and its composition remained the same. For these well relaxed samples containing Frankel pairs we independently calculated and averaged internal and free energies and compared to those of the defect-free samples. The Frenkel pair caused internal energy to change by $\Delta E_{V+I} = 3.89 \pm 0.17$ *eV* and Helmholtz free energy by $\Delta F_{V+I} = 4.58 \pm 0.16$ *eV*.

We also calculated the internal energy, entropy and Helmholtz free energy changes when an isolated vacancy is formed. To this end we randomly choose an atom in the perfect fcc Pu-3 *at.*% Ga crystal of $10 \times 10 \times 10$ unit cells and replaced it by a vacancy, so the total number of atoms was reduced by one. As in the previous calculations the averaging was done over calculations for twenty macroscopically identical samples with different distributions of