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Molecular dynamics characterization of thermodynamic and mechanical properties of Pu as dependent upon alloying additions and defects concentration. Part I

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A B S T R A C T

The paper presents results of molecular dynamics (MD) simulations which were performed to investigate mobility of defects in the δ-PuGa alloy. The defects diffuse through thermal fluctuations and MD results provided parameters for the Arrhenius law describing defect diffusion versus temperature. On the basis of this information a model of radiation defect accumulation allowing for different types of defects and grain size was constructed.The annealing of the defects at elevated temperatures and the effect of accelerated ageing due to adding small quantities of Pu-238 upon defect accumulation were evaluated.

1. Introduction

Characterization of thermodynamic and mechanical properties of materials as dependent upon alloying additions and defects concentration requires a model of defects accumulation due to self-irradiation. To construct the model one needs: (1) the data on types and the number of defects produced in collision cascades, (2) the data on the mobility of defects.

Results of MD simulation of collision cascades in Pu were reported in a number of recent papers [1–4]. In these papers different aspects of the phenomenon were investigated including characteristics of the damaged region and effects of the potential used, initial temperature, and cascade energy. Our MD simulations [1] suggest that the uranium nucleus that originates in plutonium decay and has an energy of 86 keV, causes amorphization of a compact region (8–10 nm) containing about 16000–20000 plutonium atoms. However, the crystalline structure of the damaged region almost completely recovers due to its fast annealing. Residual damages are point defects (vacancies and interstitial atoms). These are ~200 Frenkel pairs which is comparable with the number of Frenkel pairs from an alpha-particle whose initial energy is 5 MeV. The region of cascading caused by the alpha-particle is much larger in size, specifically $\sim 10^4$ nm, i.e., about 200–250 Frenkel pairs created by the alpha-particle are distributed in the larger region and almost all of them survive after the stage of fast annealing. So, primary radiation defects from the uranium nucleus and from the alpha-particle are practically equal in number. Hence the paper [1] provides us with the rate of defects production or the source of primary radiation defects. To construct a model of defects evolution one needs data on defects mobility. Partially this information is given in [5] regarding the vacancy, di-vacancy and di-vacancy dissociation. In the present work we added to [5] the data on self-interstitial, tri-vacancy and the dissociation of the latter. A tentative radiation defect accumulation model that includes the above defects and accounts for a grain size was constructed. The effect of accelerated ageing due to adding small quantities of Pu-238 upon defect accumulation was evaluated. The question about the influence of these defects upon thermodynamic and mechanical properties will be considered in the next paper.

2. Mobility of defects

Defect mobility was evaluated through straightforward MD simulations. We constructed a temperature dependence of defect jumps over certain time. Calculations for self-interstitials and tri-vacancies were performed in temperature ranges 300–600 K and 800–1000 K, respectively. Interstitials were tracked during ~100*ps* and tri-vacancies during ~30 ns. In MD calculations a sample of $\delta-$ Pu alloy ($20 \times 20 \times 20$ unit cells) containing 3 at.% of Ga was used. Interatomic interactions were described by the MEAM model with the parameter set from [6].

The resulted temperature dependencies of sedentary life were approximated by the Arrhenius law. Activation energy W and rate prefactor ζ_0 are provided in Table 1.

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Table 1
Parameters of the Arrhenius law for defect mobility.

Defect	Activation energy W (eV)	Rate prefactor ζ_0 (s^{-1})	Ref.
Interstitial atom	0.084	5.4×10^{11}	This work
Vacancy	1.06	5.0×10^{12}	[5]
Di-vacancy	1.00	6.4×10^{12}	[5]
Tri-vacancy	0.54	7.14×10^{11}	This work
Di-vacancy dissociation	1.26	5.9×10^{13}	[5]
Tri-vacancy dissociation	1.0	5.74×10^{12}	This work

3. Primary radiation defect accumulation model

The current version of the model considers defects of four types: self-interstitial, vacancy, di-vacancy and tri-vacancy. The last two may dissociate. It will become clear from what follows why we restricted ourselves to these defects. Below is a system of equations that describes how the system of defects evolves with time. The equations were written from the assumption that self-irradiation and subsequent fast annealing leave only single vacancies and interstitial atoms (see [1]).

$$\begin{aligned}
\frac{dn_i}{dt} &= -\chi_i n_v n_i - 2\chi_i n_{2v} n_i - 3\chi_i n_i n_{3v} - \beta_i n_i + S_i \\
\frac{dn_v}{dt} &= -\chi_i n_v n_i + 2\chi_i n_{2v} n_i - 2\chi_v n_v^2 - \chi_{2v} n_{2v} n_v - \beta_v n_v \\
&\quad + 2\chi_{dis2v} n_{2v} + \chi_{dis3v} n_{3v} + S_v \\
\frac{dn_{2v}}{dt} &= -2\chi_i n_{2v} n_i + \chi_v n_v^2 - \chi_{2v} n_{2v} n_v + 3\chi_i n_i n_{3v} - \beta_{2v} n_{2v} \\
&\quad - \chi_{dis2v} n_{2v} + \chi_{dis3v} n_{3v} \qquad (1) \\
\frac{dn_{3v}}{dt} &= -3\chi_i n_{3v} n_i + \chi_{2v} n_{2v} n_v - \beta_{3v} n_{3v} - \chi_{dis3v} n_{3v},
\end{aligned}$$

where n_k = defect concentration, S_k = source defined by the rate of radioactive decay, β_k = drain rate on grain boundaries, and χ_k = rate of defect annihilation or nucleation in interaction with another defect. In calculations, it was assumed that $S_i = S_v = 400$ *vacancies(IA)/decay*. The rate χ_k is chosen from characteristics for the more mobile defect. For example, for the annihilation of a vacancy and an interstitial, χ is calculated from the interstitial characteristics: $\chi_i = 1/(n_{Pu}\tau_i)$, where n_{Pu} – concentration of Pu atoms at ambient conditions and τ_i is the interstitial mobility ($\tau = 1/\zeta$).

Defect drains are calculated from the following considerations. When a defect appears near a boundary at a distance of one jump, it is absorbed by the boundary with probability 0.5. The fraction of defects in a layer of thickness $a/2$ (a = unit cell parameter) is equal to $(a\Omega_G/2V_G)$, where Ω_G and V_G are, respectively, grain surface and grain volume. Then $(a\Omega_G/2V_G)n_k/2\tau_k$ defects of type k will be absorbed per unit time, i.e., $\beta_k = (a\Omega_G/2V_G)/2\tau_k$. In the calculations presented below, the grain size was taken to be $\xi = 20$ μm and grain surface and volume were, accordingly, $\sim\xi^2$ and $\sim\xi^3$.

Fig. 1 shows a solution of (1) for delta-PuGa (3 at.% Ga) with the initial conditions $\{n_k\} = 0$. It is seen that the system of defects gets equilibrium in about 3–4 years. The system consists of mainly vacancies whose concentration reaches ~0.1%. The concentrations of other defects are several orders of magnitude lower. In this figure we also plotted the data obtained with the vacancy activation energy which is 5% lower than that cited in Table 1. Thus, the effect of an error in W_v is demonstrated.

Solutions were also obtained for systems which included (1) only vacancies and IA; (2) vacancies, di-vacancies and interstitials; and (3) vacancies, di-vacancies, tri-vacancies and IA. They are shown in Fig. 2 as the dependence of vacancy concentration on time. The dependencies for other defects are not provided because their numbers are several orders of magnitude smaller in all cases. It is seen from Fig. 2 that the consideration of di-vacancies results in a much smaller (about 5 times) number of dominating defects – vacancies. Merging into more mobile di-vacancies, the vacancies more intensively drain on grain boundaries. Adding tri-vacancies is of a much smaller effect on the decrease of vacancies, no more than 10%. That is why we limited our consideration of defects to tri-vacancies. It is also seen from Fig. 2 that the consideration of vacancy clustering changes the equilibration time, reducing it to about 3–4 years.

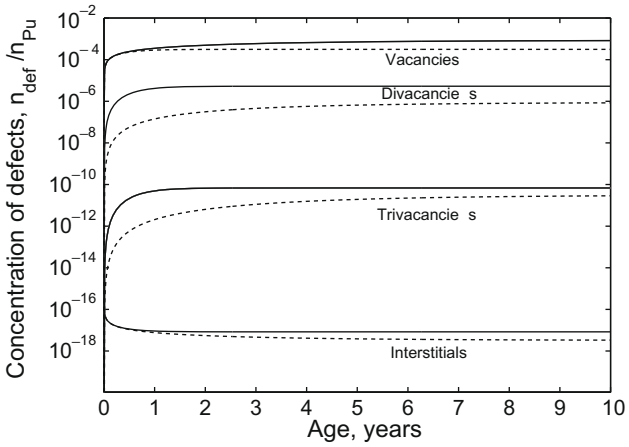

Fig. 1. Evolution of primary radiation defects with time at $T = 300$ K. Solid lines – $W_v = 1.06$ eV, dashed line – $W_v = 1.0$ eV.

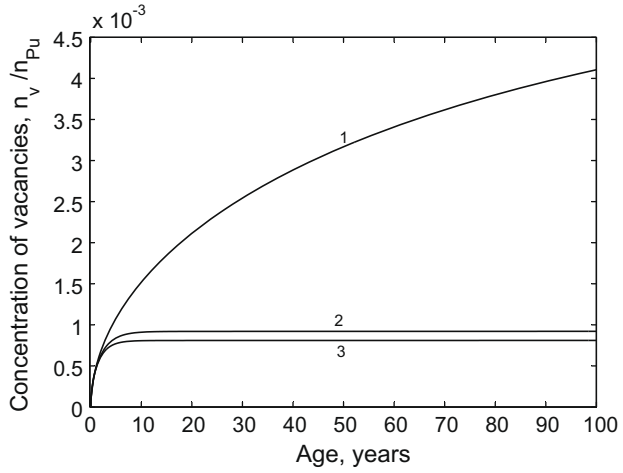

Fig. 2. Concentration of vacancies versus time for taken into account vacancies and interstitials (curve 1); vacancies, di-vacancies and interstitials (curve 2); and vacancies, di-vacancies, tri-vacancies and interstitials (curve 3).

Data on the time evolution of primary radiation defects agree with experimental data on changes in plutonium properties during the first years of storage (see [7,8]). So, Ref. [7] provides experimental results on changes in the volume of PuGa (2 at.% Ga) samples in ageing. These results were obtained with the use of accelerated ageing. Pu-238 (7.38 at.%) was added to the alloy and self-irradiation proceeded ~22 times faster.

Fig. 3 depicts dilatometry measurements from [7]. For all samples and measurement temperatures, the initial period of volume

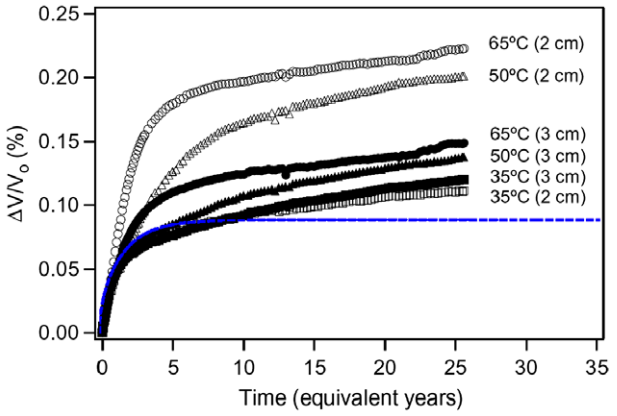

Fig. 3. Relative change in the volume of Pu-238 enriched PuGa [7]. Time is measured in equivalent years. Measurements were done for 2 samples (2 and 3 cm) hold at different temperatures. According to [7], data for 35 °C are most reliable because surface effects at this temperature are weak and results for 2-cm and 3-cm samples coincide (see [7] for details). The dashed line shows calculation with the model proposed.

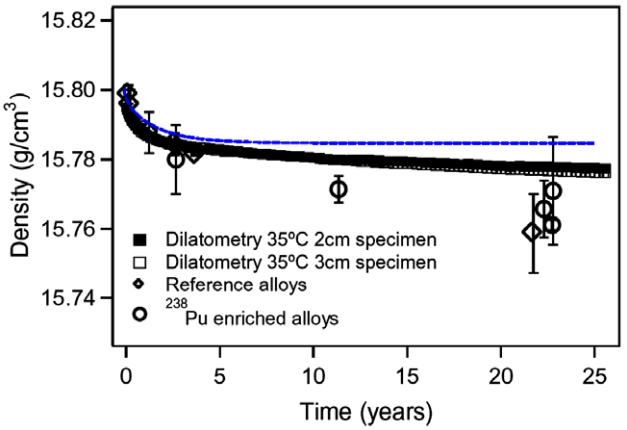

Fig. 4. Density changes: dilatometry of the enriched plutonium sample (35 °C), immersion of naturally aged and Pu-238 enriched samples (the data taken from [7]). The dashed line shows calculations with the model proposed.

increasing is seen to be ~3–4 years; then the curve flattens out with a weak linear growth which is associated with the constant rate of helium accumulation. The dashed line in Fig. 3 shows the relative change in volume evaluated in this work in the assumption that it equals the relative concentration of vacancies. It is of course an upper estimate so as we assumed all interstitials that were absorbed by the grain boundary were built into the structure without changes in density.

Fig. 4 compares changes in density with time, obtained experimentally through dilatometry and immersion measurements for different plutonium samples and predicted by the model proposed.

This volumetric change is known as transient reverse expansion, i.e. it can be eliminated by annealing that reduces the equilibrium concentration of defects. The proposed model of defect accumulation is capable of simulating annealing using the constructed dependence of defect mobility on temperature. Fig. 5 shows how the concentration of defects (vacancies) varies with time in annealing at different temperatures. The initial state corresponds to the equilibrium concentration at $T = 300$ °C. According to these data, it takes primary radiation defects about 2 h to anneal at ~220 °C. During this time the concentration of defects reduces from ~0.1% to ~0.00001%. This is also in agreement with the known experimental evidence (see, for example, [8]) that the density changes that occur in the first three years of storage can easily be recovered through annealing at 150–200 °C.

One more issue that deserves consideration is adequacy of extending the accelerated ageing data to naturally aged material.

In this report we touch only defects associated with primary radiation damage. As shown above by predictions, single vacancies are main contributors to the system of defects. The concentration of other defects is negligible. Consider, for example, a material enriched with 5 at.% Pu-238. The intensity of self-irradiation becomes 15 times higher. Accordingly increasing the source in the system of Eq. (1), we obtain (see Fig. 6) that the equilibrium concentration of defects increases by a factor of about 3 (curve 1) if compared to natural ageing (curve 3), while the equilibration time decreases.

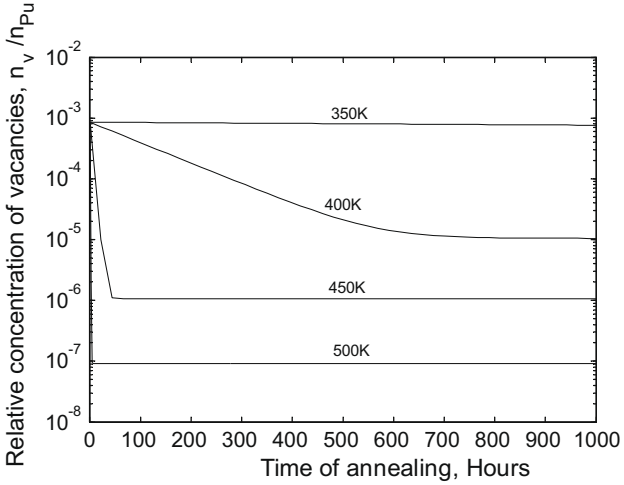

Fig. 5. Concentration of defects (vacancies) versus time in annealing. The initial state corresponds to the equilibrium concentration at $T = 300$ °C.

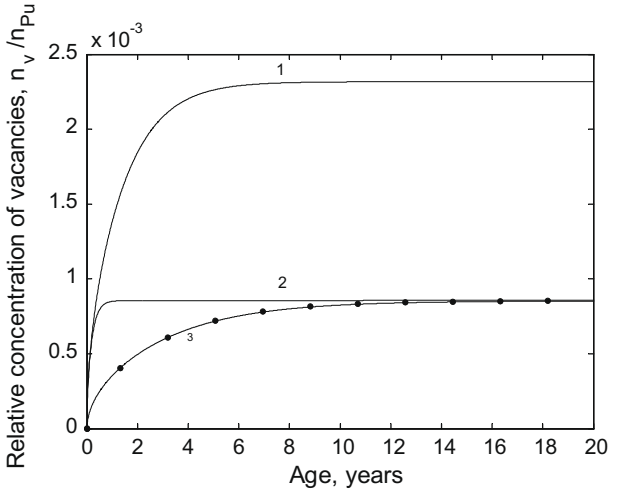

Fig. 6. Concentration of vacancies versus time. Curve 1: accelerated ageing (5 at.%Pu-238) at 300 K; curve 2: accelerated ageing (5 at.% Pu-238) at 322 K; curve 3: natural ageing at $T = 300$ K. The circles – accelerated ageing at 322 K: vacancy concentration is plotted versus equivalent years, i.e., the time scale is multiplied by the factor of acceleration (~15).

To get to the state of the system (in the defect concentration sense) corresponding to naturally aged material, it is necessary to increase defect mobility, i.e., the temperature of sample holding. As shown in Fig. 6, when the temperature increases from 300 K to 322.5 K (curve 2), the concentration of defects decreases to the level of natural aging at 300 K. The rate of defect accumulation in enriched material at 322.5 K appears to be exactly 15 times higher. Indeed, as it is demonstrated in Fig. 6 if one uses equivalent years for enriched material stored at 322.5 K, i.e. time axis is multiplied by the factor of acceleration ~15 (corresponding data are pointed in Fig. 6 with black circles) then defect accumulation coincides with natural ageing (curve 3).

Explaining transient, reversible expansion by the accumulation of defects from the displacement damage we should note the experimental fact that the length change is less than the lattice parameter change (see for example [8]). But if the dimensional changes were due to the radiation defects only the length change should be equal to or greater than the lattice parameter change.

In [9] another mechanism that could be responsible for density and lattice parameter change was explored. Namely, MC simulations of PuGa alloys showed Ga short ordering and segregation leading to formation of Ga-rich and Ga-poor regions. In our opinion assuming linear dependence of lattice parameter upon Ga concentration in fresh material one may conclude that the segregation does not lead to density change but may affect lattice parameter measured through XRD. One more mechanism was proposed in [8] where transient reversible expansion is explained by incipient precipitation of ζ'-phase (Pu_3Ga) that occupies a smaller volume per atom than Ga-stabilized $\delta - Pu$. The precipitation of ζ'-phase depletes the surrounding $\delta - Pu$ alloy of gallium atoms increasing its lattice parameter. The interplay of these processes provides for the experimental fact that the length change is less than the lattice parameter change. Finally, in [10] an evidence for α'-phase embryos was found. The embryos were associated with regions locally depleted in Ga.

Here we demonstrated that the accumulation of radiation defects may play an important role in the material property changes during the first 3–4 years. Probably, combining effects from radiation damage described here, Ga segregation [9], and α'-phase embryos formation [10] it will be possible to explain density and lattice parameter change, but careful evaluation of the combined effect requires additional data on the rate of Ga segregation and conditions for α'-phase precipitation.

4. Conclusion

Our calculations gave the dependence of primary radiation defect concentration on time. The transient (equilibration) time was shown to be about 3–4 years which agrees well with the available experimental data [7,8] on specific volume changes. It is also known from experiment that this transient process is reversible: the material recovers its initial state after several hours of annealing at ~200 °C [8]. This is also in agreement with the predictions obtained in this work.

It has also been shown that for the adequate extension of results obtained for accelerated ageing to natural ageing, Pu-238 enriched samples need holding at elevated temperatures. So, for an enrichment of 5 at.% Pu-238, the temperature must be increased by 22 °C. In this case accelerated ageing (concentration of primary radiation defects) will correspond to natural with a time scale factor of 15.

It should be noted that the results we presented here are purely theoretical. All parameters for the defect evolution model were obtained in MD simulations.

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