ELSEVIER

Journal of Alloys and Compounds 444–445 (2007) 310–313

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

# Computer simulation study of self irradiation in plutonium

Gérald Jomard [a,*], Lilian Berlu [b], Gaëlle Rosa [b], Philippe Faure [b], Jérôme Nadal [b], Nathalie Baclet [b]

[a] *CEA DIF/DPTA, F-91680 Bruyeres le Châtel, France*
[b] *CEA VA/DRMN, F-21120 Is sur Tille, France*

Received 5 July 2006; received in revised form 16 October 2006; accepted 17 October 2006
Available online 8 December 2006

**Abstract**

There is clear experimental evidence that plutonium based materials exhibit density changes with time. By comparison to what is known for nuclear fuel cell aging, it is believed that this phenomenom could be linked to the radioactive α-decay of plutonium. Schwartz et al. have identified three possible age-related phenomena due to self irradiation in Pu alloys that would cause dimensional changes: the initial transient, helium accumulation and void swelling [A.J. Schwartz, M.A. Wall, T.G. Zocco, W.G. Wolfer, Philos. Mag. 85 (2005) 479]. Even if the later phenomenon has not yet been observed in naturally aged Pu alloys, the aim of this work is to examine its possible occurrence by means of a multi-scale modelling approach. We coupled classical molecular dynamics simulations (MD) to mesoscopic Monte Carlo ones (MMC) in order to predict the long-term evolution of point defects created by self irradiation in plutonium. In this article, we focus on the results obtained for the MD radiation damage simulations. We show that plutonium does not seem to behave like other metals under ion irradiation. The annealing process of the defects produced by a recoil nucleus is indeed very long compared to what is known for various other metals. An MD parametric study of displacement cascade simulations combining temperature and cascade energy will be exposed. At the end, we will present results of preliminary MMC simulations based on our MD data which show that the spatial correlation of the stable defects populations created by the cascades seems to have a great influence on the predicted swelling.


*Keywords:* Pu; Radiation damage; Annealing; Molecular dynamics; Monte Carlo

## 1. Introduction

In all plutonium based materials, the α-decay of plutonium nuclei is responsible for the creation of numerous point defects in the crystal. The way these primary defects evolve may give rise to important changes in the structural properties of the material. As an example, swelling of plutonium alloys has been experimentally observed with various techniques (dilatometry and X-ray diffraction) [1–4]. But it is not clearly established yet if this phenomenon is linked to the radioactive property of plutonium. One reason is that the radioactivity and toxicity of plutonium are limiting drawbacks to extensive experimental measurements. Predicting the long-term effects of self irradiation in plutonium based materials is thus a real challenge for simulation. To reach this goal, we have developed a multi-scale approach based on classical MD simulations coupled to event-based Monte Carlo calculations. Obviously, there is a strong interplay between experiments and the theoretical approach in order to parametrize and validate the various models we used. This work is an extension of a previous study of damage production in Pu [12]. We had compared the development of 2 keV collision cascades in plutonium predicted by both the Embedded Atom Method (EAM) and the Modified EAM (MEAM) methods [11,6]. Since the MEAM formalism is the more reliable one to capture the unusual physical properties of Pu, we continued this study in this framework. In this paper, we will show that the predicted void swelling in plutonium is sensitive to the spatial configuration of the defects populations obtained by MD. Once again, we should mention that this part of our work is purely prospective since at this point, there is no experimental evidence that void swelling occurs in Pu-based materials.

## 2. Computational details

The MEAM formalism of Baskes has been implemented in our MD code STAMP which is designed for use on massively

* Corresponding author.
*E-mail address:* gerald.jomard@cea.fr (G. Jomard).

0925-8388/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2006.10.157

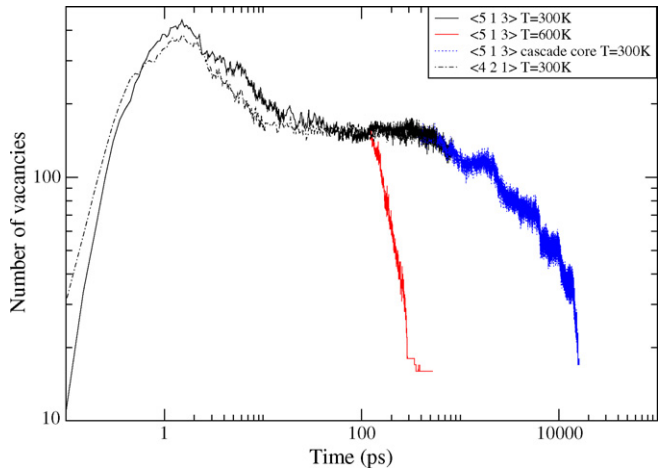


Fig. 1. This figure represents the number of vacancies created by the cascades vs time for a 2 keV PKA.

parallel machines [6]. An efficient parallelization based on MPI with a 3-D spatial decomposition scheme allows one to treat systems of millions of atoms. In order to simulate high energy cascades, we have modified the repulsive part of the original potential from Baskes to provide a better treatment of atomic interactions for small distances. For that purpose, we used the universal Kr–C potential of Wilson and coworkers [9], which is smoothly joined to the MEAM potential with a polynomial exponential of order 3 between 1 and 2 Å. More details on this procedure can be found elsewhere [10]. To model the defect production, we follow the usual procedure. An fcc crystal of plutonium is first equilibrated at $T = 300$ K in the statistical microcanonic thermodynamical ensemble (NVE). Then an atom located near the center of the simulation cell is chosen to play the role of the primary knock-on atom (PKA). A kinetic energy $E_{PKA}$ is given in a desired crystallographic direction to this atom to model the emission of a recoil nucleus that initiates a collision cascade.

## 3. Defect production results

In order to provide reliable data to the mesoscopic models, we need a correct statistics on the predicted damage production. We have thus varied the PKA energy and its initial directions in our simulations. The $\langle 4, 2, 1\rangle$ and $\langle 5, 1, 3\rangle$ directions have been explored for 2 keV cascades, and the $\langle 4, 2, 1\rangle$, $\langle 5, 1, 3\rangle$, $\langle 10, 5, 2\rangle$ and $\langle 10, 2, 5\rangle$ ones have been studied for 10 keV cascades. Since the observed trends are very similar for all these simulations we will focus on the 2 keV cascades results. The evolution of the computed number of vacancies versus time is plotted in a log–log scale in Fig. 1.

We can see that the initial direction of the PKA has almost no effect on the defects production. The maximum number of Frenkel pairs created is more or less the same and this value is reached in both cases after 1.5 ps. For both directions, the development of the cascade leads to the formation of an amorphous zone in the crystal. It is surprisingly stable for many nanoseconds, the cooling stage is thus extremly long compared to what is known from other fcc metals (in Cu, Au and Pb for example, the cooling stage lasts only a few tens of picoseconds [13,14]). This is far from usual for a fcc metal and is more likely observed for semi-conductors materials [5]. As suggested by Valone et al., this phenomenon may be explained by the fact that the MEAM potential exhibits a lot of minima because of its ability to describe all the crystal structures of plutonium. Atoms can thus be frozen temporarily in amorphous-like atomic arrangements. This assumption should be tested by doing MD simulations with

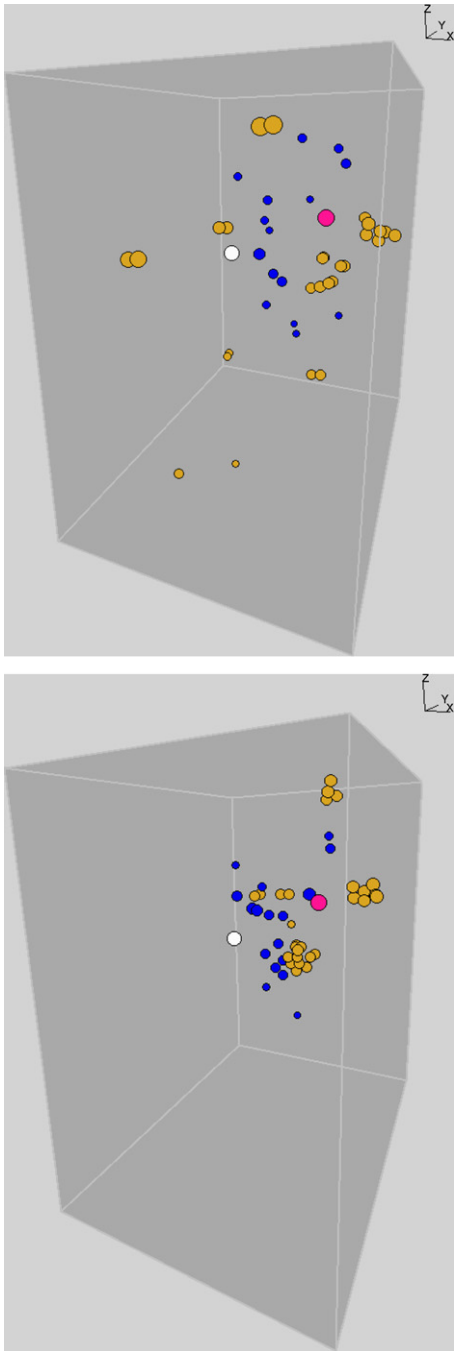

Fig. 2. Stable defect population for a 2 keV cascade simulated with the MEAM potential in the $\langle 5, 1, 3\rangle$ initial direction for the PKA. (Top) picture corresponds to $t = 300$ ps of the simulation where the cell is heated at $T = 600$ K. (Bottom) picture corresponds to $t = 15$ ns of the simulation at $T = 300$ K. Only vacancies (in blue), single insterstitials and dumbells (in orange) are represented.

the Pu–Ga MEAM potentials of Baskes and coworkers [7,8] which is able to reproduce room temperature stabilization of the δ phase.

In order to reduce the computational time required to anneal the defects produced by a cascade within MEAM, we have tried to accelerate the kinetics of the recombination process by heating the simulation cell up to 600 K. During the same time, we extracted the core part of our cascades after 120 ps and followed their evolution until the stable defects population was achieved at 300 K.

When the simulation cell is heated (after around 120 ps at 300 K), we observe in Fig. 1 that the stable defect configuration is reached in only 400 ps. We found that the number of defects at the end of the annealing procedure is quite similar to what is obtained at $T = 300$ K when extracting the core part of the cascade (see Fig. 2). Vacancies are mainly isolated, no cluster is observed while small clusters of interstitials are present. We must note that even if the spatial repartitions of defects of Fig. 2 are similar they are not really identical. We can especially see that at $T = 600$ K interstitials move farther away from the core of the cascade than at room temperature. This is not surprising because of the very small migration energy of such point defects [15,10]. We will see in the following that this slight difference of spatial defects repartition could be of primary importance for predicting the long-term behavior of the defects.

At least the main result of all our collision cascade simulations is that vacancies are not clustering. This is in agreement with cohesive energy calculations for simple defects, such as di- or tri-vacancies which show essentially no bonding [10]. Moreover clustering is not likely to occur at long time since the vacancy migration energy is relatively high, around 0.8 eV according to our calculations [10]. Recently, Fluss et al. studied the temperature-dependent defect properties from ion-irradiation in δ-PuGa by electrical resistivity measurements during isochronal-annealing of damage accumulated. They argue that interstitial clustering is extant for self irradiation, but that the corresponding vacancies from the uranium damage cascade appear to be more point defect-like [17]. This seems to corroborate our findings for the spatial repartition of defects created by 2 and 10 keV cascades in pure plutonium.

## 4. A preliminary study of long-term evolution defects by mesoscopic Monte Carlo simulations

Our goal is to study the macroscopic physical properties modifications induced by self irradiation in plutonium-based materials. The idea is to use event-based Monte Carlo simulations for which the source of defects will be the final configurations obtained by MD. We used the code JERK developed at CEA/DEN/SRMP by Dalla Torre et al. [16]. To be realistic this approach should include results for 85 keV cascades that we do not have these yet. So we have decided to start with a parametric study with results for 2 keV cascades either heated or not in order to examine the sensitivity of the long-term vacancy-based swelling with respect to the input spatial configuration of the defects populations. The various events that are taken into account in our simulations are : creation of defects by inclusion of the stable defects populations obtained by MD, annihilations of vacancies (V) and interstitials (I), dissociations of defects (that means emission of V, 2-V or 3-V from $n$-V clusters and emission of I from $n$-I clusters), absorption of defects on initial dislocations lines eventually present in the box. We do not allow vacancy emission from dislocation lines. Only mono-vacancies, single- and di-interstitials are mobile in our model. The various parameters used in this study are summarized in Table 1.

We performed mainly two sets of simulations. In the first one we used defect populations obtained either at 300 or 600 K, and either the stable populations or populations picked up after 150 ps in our MD runs. The second set of simulations consisted of studying the difference of swelling induced by an homoge-

Table 1
Various input parameters used in our MMC simulations

| | |
|---|---|
| Creation rate of primary damage defects (2 keV cascade) | $\Phi = 3.2\text{e}{-9}\ \text{dpa}\,\text{s}^{-1}$ |
| Temperature | $T_{\text{melting}}/3$ |
| Lattice parameter | $a_0 = 4.61$ Å |
| Initial dislocation density | $1.0 \times 10^{12}\ \text{cm}^{-2}$ |
| Interaction radii | $R_{\text{VI}} = R_{\text{IV}} = R_{\text{II}} = R_{\text{VV}} = 1.81a_0$ and $R_{\text{V}}^{\text{dislo}} = R_{\text{I}}^{\text{dislo}} = 22.85 \times 10^{-3}a_0$ |
| Bias factors | $Z_{\text{VI}} = Z_{\text{IV}} = Z_{\text{VV}} = 1$, $Z_{\text{II}} = 1.2$ and $Z_{\text{V}}^{\text{dislo}} = Z_{\text{I}}^{\text{dislo}} = 1$ |
| Vacancy radius | $R_{\text{V}} = 0.3908a_0$ |
| Diffusion frequency factor | $D_{0\text{V}} = 1.5 \times 10^{-8}\ \text{cm}^2\,\text{s}^{-1}$ |
| Energy of migration | $E_{\text{V}}^{\text{m}} = 0.4$ eV |
| Energy of formation | $E_{\text{V}}^{\text{f}} = 0.5$ eV |
| Binding energy of two vacancies | $E_{2\text{V}}^{\text{b}} = 0.2$ eV |
| Interstitial radius | $R_{\text{I}} = 0.3908a_0$ |
| Diffusion frequency factor | $D_{0\text{I}} = 1.0 \times 10^{-12}\ \text{cm}^2\,\text{s}^{-1}$ |
| Energy of migration | $E_{\text{I}}^{\text{m}} = 0.05$ eV |
| Energy of formation | $E_{\text{I}}^{\text{f}} = 2.3$ eV |
| Binding energy of two interstitials | $E_{2\text{I}}^{\text{b}} = 0.9$ eV |
| Diffusion frequency factor | $D_{02\text{I}} = 5.0 \times 10^{-13}\ \text{cm}^2\,\text{s}^{-1}$ |
| Energy of migration | $E_{2\text{I}}^{\text{m}} = 0.05$ eV |

neous defect source (Frenkel pairs are introduced in the box) or by a cascade-type defect source.

This preliminary study shows that:

- MMC predicted swelling is very sensitive to the spatial configuration of defects populations taken from MD simulations. Indeed, we found a discrepancy of one order of magnitude between the swelling induced by 300 K cascades and 600 K ones.
- The swelling obtained with a 2 keV stable defect population (for $T = 300$ K) source is 30% lower than what is found with an homogeneous defects source.

One has to keep in mind that these preliminary results can only give trends for the moment. They have to be confirmed by a more realistic study since some input parameters of our Monte Carlo simulations were not specific to plutonium.

## 5. Conclusion

This work is a part of a general multi-scale modelling approach that aims at describing self irradiation effects in plutonium alloys. A parametric study of molecular dynamics displacement cascade simulations has been done to get intrinsic properties of defects population produced by self irradiation: the number of defects, the number and size of clusters, spatial repartition and spatial expansion of the cascade as a function of PKA energy and direction. Our results show in particular that the defects recombination stage is much longer than in other metals. The vacancies do not seem to form clusters which is in agreement with the experimental results of Fluss et al. [17]. Our preliminary study of the long-term evolution of primary defects created by cascades by means of Monte Carlo simulations show that the predicted swelling is very sensitive to the spatial configuration of defects populations.

## References

[1] O. Chebotarev, O. Utkina, Plutonium and Other Actinides, North-Holland Publishing Company, 1976, p. 599.
[2] W.G. Wolfer, Los Alamos Sci. 26 (2000) 275.
[3] B. Oudot, Ph.D. Thesis, Université de Franche-Comté, Besançon, France, 2005.
[4] G. Rosa, B. Ravat, L. Jolly, B. Oudot, L. Berlu, V. Klosek, J.L. Flament, N. Baclet, P. Faure, G. Jomard, Actinides (2005).
[5] K. Nordlund, M. Ghaly, R.S. Averback, M. Caturla, T. Diaz de la Rubia, J. Tarus. Phys. Rev. B 57 (1998) 7556.
[6] M.I. Baskes, Phys. Rev. B 62 (2000) 15532.
[7] M.I. Baskes, K. Muralidharan, M. Stan, S. Valone, F.J. Sterne, JOM (2003).
[8] S.M. Valone, M.I. Baskes, R.L. Martin, Phys. Rev. B 73 (2006) 214209.
[9] L.G. Haggmark, W.D. Wilson, J.P. Biersack, Phys. Rev. B 15 (1977) 2458.
[10] L. Berlu, G. Rosa, P. Faure, G. Jomard, J. Nucl. Mater., submitted for publication.
[11] P. Pochet, Nucl. Instrum. Methods B 202 (2003) 82.
[12] G. Jomard, P.M. Anglade, Proceedings of the Third International Conference on "Computational Modeling and Simulation of Materials", Acireale, Sicily, 2004.
[13] D.J. Bacon, A.F. Calder, F. Gao, J. Nucl. Mater. 251 (1997) 1.
[14] D.J. Bacon, F. Gao, Yu N. Osetsky, J. Nucl. Mater. 276 (2000) 1.
[15] S.M. Valone, M.I. Baskes, J. Nucl. Mater. 324 (2004) 41.
[16] J. Dalla Torre, J.-L. Bocquet, N.V. Doan, E. Adam, A. Barbu, Philos. Mag. (2005) 85.
[17] M.J. Fluss, B.D. Wirth, M. Wall, T.E. Felter, M.J. Caturla, A. Kubota, T. Diaz de la Rubia, J. Alloys Compd. 368 (2004) 62.