Journal of Nuclear Materials 385 (2009) 75–78

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Molecular dynamics simulation of helium–vacancy interaction in plutonium

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ARTICLE INFO

PACS:
61.72.–y
61.72.Cc
61.72.Qq
71.15.Pd

ABSTRACT

The formation energies of small He_nV_m clusters (n and m denote the number of He atoms and vacancy, respectively) in Pu have been calculated with molecular dynamics (MD) simulations using the embedded atom method (EAM) potential, the Mores potential and the Lennard–Jones potential for describing the interactions of Pu–Pu, Pu–He and He–He, respectively. The binding energies of an interstitial He atom, an isolated vacancy and a self-interstitial Pu atom to a He_nV_m cluster are also obtained from the calculated formation energies of the clusters. All the binding energies mainly depend on the He–vacancy ratio (n/m) of clusters rather than the clusters size. With the increase of the n/m ratio, the binding energies of a He atom and a Pu atom to a He_nV_m cluster decrease with the ratio, and the binding energy of a vacancy to a He_nV_m cluster increases. He atoms act as a catalyst for the formation of He_nV_m clusters.

1. Introduction

Pu is perhaps the most complex metallic element known and has attracted extraordinary scientific interest since its discovery in 1941. It is of great technological importance due to its use in nuclear industry. However, modern day problems concerning Pu involve understanding and predicting the properties of Pu and its alloys for the safe handling, use and long-term storage of these important, but highly toxic materials which made experimental observations extremely difficult [1]. So, development of a predictive aging model for plutonium is one of major goals of many researchers' works on Pu. Pu is vulnerable to aging because it is a radioactive element, decaying to U by emitting α particle. Although the widely used Pu-239 has a relatively long half-life of about 24000 years, its decay rate is still sufficiently high to lead to a significant buildup of He and radiation damage within the metal after several decades [2]. As for the behavior of He atoms in Pu lattice, there may be a number of interactions occurring in the lattice. These interactions include (a) trapping and thermal detrapping of He atom in single vacancy, divacancies, and vacancy clusters; (b) He atom trapping at dislocations and grain boundaries; (c) replacement of He atom bound to single vacancy by either interstitial Pu atoms or U atoms or other impurities; (d) He atom clustering into He–vacancy clusters and He bubble; (e) displacement of trapped He atoms by He-He or He–U collisions; and (f) diffusion of He atom as an interstitial [3]. As is well known, He in metals can produce macroscopic effects such as swelling and embrittlement, thus alter the properties of metals and alloys. Pu–He system may be a very typical example [2].

Despite some research regarding He effects with direct and indirect techniques in Pu there are still many unknowns [4–7], especially regarding the initial stages of nucleation of such defects as bubbles and voids. In terms of Trinkaus's classification of He bubble by size, the lowest size class is usually indicated by He_nV_m clusters, which may play an important role in the nucleation of He bubble [8,9]. Such small He_nV_m clusters are hardly characterized experimentally, which should be necessary for a theoretical approach. In order to obtain further knowledge about the initial stage of He_nV_m cluster or He bubble nucleation, MD simulations are performed to investigate the problem.

2. Computational method

The relatively straightforward way to address the atom-level behaviors of He in metals is to use the MD technique. Such a calculation describes the evolution of the system with time, based on a direct numerical solution of the equations of motions for individual atoms. Of critical importance for a successful performance of MD is a precise and computer efficient description of interatomic interactions. For the atomic interaction, three potentials are employed in the present calculations. To describe the interaction between Pu atoms, we have developed and used our own MAEAM potential of fcc δ Pu to carry out MD simulation of small helium bubbles in Pu [10]. EAM is a popular and effective approach for modeling the properties of metallic solids while studying extended defects or other situations in which the size of the required crystalline unit cell is too large for ab initio electronic structure calculations, or

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doi:10.1016/j.jnucmat.2008.09.034

when very many time steps would be required in a dynamic simulation. In addition, the interaction potential for He–He is the Lennard–Jones potential and He–Pu potential is Morse potential which are been used to study the He effects in Pu [10].

Three-dimensional periodic cell of $10a_0 \times 10a_0 \times 10a_0$ is used (a_0 is the lattice constant) to calculate the formation energy of small He_nV_m cluster. The structure of the empty void is determined by beginning with a single vacancy, and repeatedly removing the atom having the highest potential energy from the cell, thereby creating another vacancy for calculating the isolated vacancy formation energy, so the formation energy of divacancy is calculated. By repeating the step in the same manner, the vacancies are increased one by one and the formation energy of an empty void is obtained as a function of the number of vacancy in the void. Afterwards, a He atom is firstly introduced into an m-size void V_m for calculating the formation energy of He_1V_m cluster, then the He atoms are introduced into the cluster one by one for calculating the formation energies of the clusters containing increasing He atoms. In order to fully relax the atoms, annealing molecular dynamics is employed. The computational system is relaxed at 300 K, with the temperature controlled via explicit rescaling of the velocities and the pressure controlled using Parrinello and Rahman method [11,12], followed by slowly cooling and quenching the system to 0 K. The positions of the atoms are relaxed to their minimum energy configurations. The time step used is 10^{-15} s and the total simulation time is 10^{-11} s, i.e. 10000 steps. The forces exerted on each atom are calculated, and then the formation energies of He_nV_m clusters are calculated. The definitions of formation energy and binding energy of He_nV_m clusters can be referred to the literature [9].

3. Results and discussion

3.1. Formation energies of empty voids

It is well known that He atom prefers to occupy the sites with low electron density mainly due to its filled-shell electronic configuration. Clearly, the vacancy-type defect such as empty void should be a likely place for He atoms to fill. Using the simulation approaches as described in the previous discussion, we have calculated the void formation energies without He atom.

Fig. 1 shows the plots of void formation energies and the binding energy of the nth vacancy to the void versus the number of vacancies in void in Pu. As shown in the figure, the total formation energies of voids increase with the increase of the number of vacancies. There are some maximums in the plot of vacancy binding energy versus the number of vacancies, from which we can conclude that those voids having higher vacancy binding energy are energetically favorable than single vacancy or other voids, and those voids may be more likely places for the He atom to fill. We consider that the stability of void is related with the structure and number of vacancy. Further works will be carried out on the stability of void in detail. However, the largest value of the vacancy binding energy does not exceed 0.8 eV. The vacancy binding energy is dramatically changed when He atoms are introduced into the voids, as mentioned in the followings, the maximal vacancy binding energy is about 3.0 eV.

3.2. Formation energies of He_nV_m clusters

The formation energies of He_nV_m clusters are the foundation of calculating the defect binding energies. Fig. 2 shows the dependence of the formation energies of He_nV_m clusters on the number of He atoms. It can be found that for He atom in Pu lattice, the formation energies of He_nV_m clusters slowly increase with the introducing of He atom until the ratio of the number of He atom to vacancy is greater than 1, which indicates the lowest energy configuration occurs when there is one vacancy per He atom. Fig. 3 shows the dependence of the formation energies of He_nV_m clusters on the number of vacancies. The formation energies of He_nV_m clusters slowly decrease with the introducing of vacancy until the ratio of the number of He atom to vacancy is greater than 1, which also indicates the lowest energy configuration occurs when there is one vacancy per He atom. When the He-to-vacancy ratio (n/m) of a cluster is less than 1, the formation energy of the cluster is close to the void formation energy. However, when $n/m > 1$, the rapid increase of the formation energy is mainly due to the presence of He. In this way, the cluster size dependence of the formation energy of a He_nV_m cluster is greatly dependent on the ratio, n/m [9,13,14].

3.3. Binding energies of a He atom, a Pu atom and a vacancy to He_nV_m clusters

According to the definition of defect binding energy, the binding energies of a He atom, a Pu atom and a vacancy to a He_nV_m cluster have been calculated. These binding energies of He and vacancy are graphed in Fig. 4 and Fig. 5, respectively. He density is defined as the He-to-vacancy atomic ratio of the He_nV_m cluster, which is provided by n/m.

As shown in the two figures, the binding energies show a strong dependence on the He density. He binding energy represents the

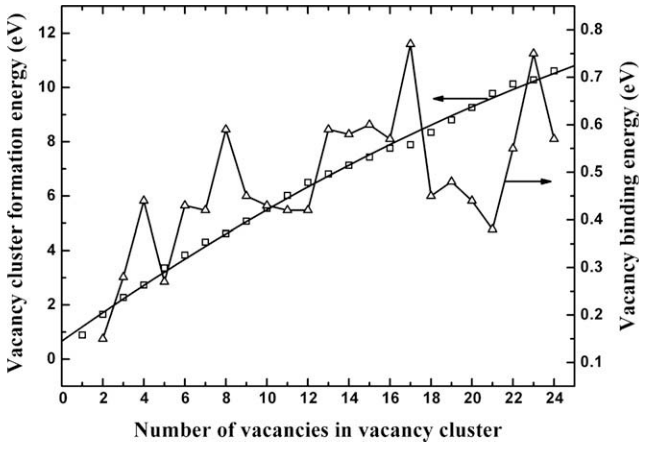

Fig. 1. Void formation energy and vacancy binding energy as a function of the number of vacancies.

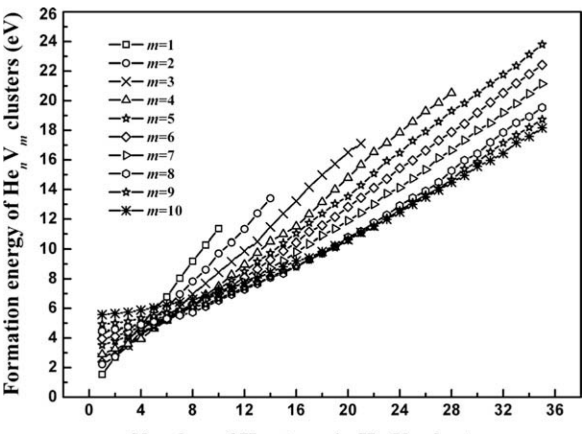

Fig. 2. He_nV_m formation energy as a function of the number of He atoms.

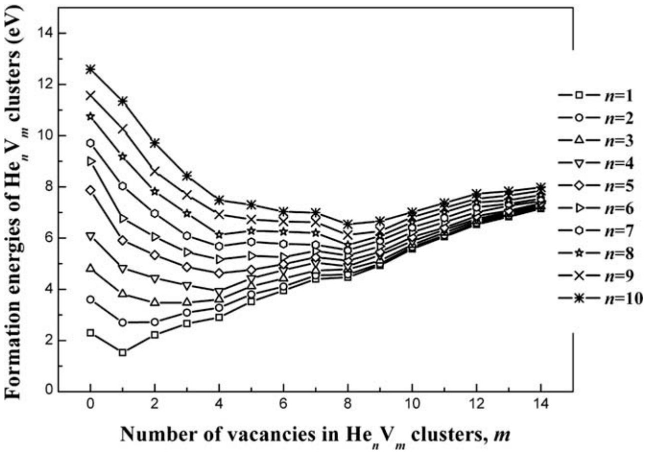

Fig. 3. He$_n$V$_m$ formation energy as a function of the number of vacancies.

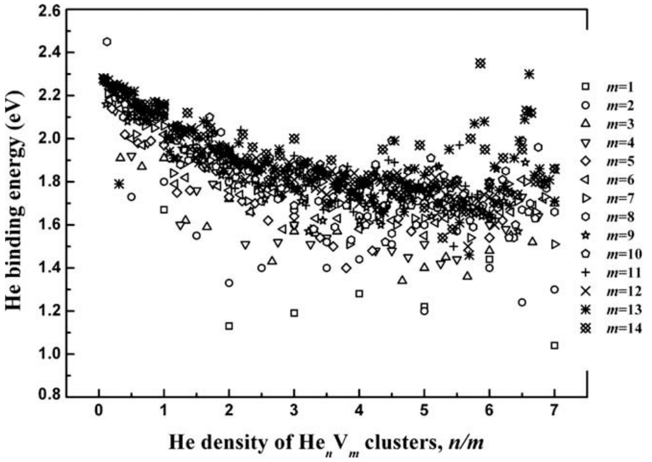

Fig. 4. The binding energy of a He atom to He$_n$V$_m$ clusters as a function of the He density of the clusters.

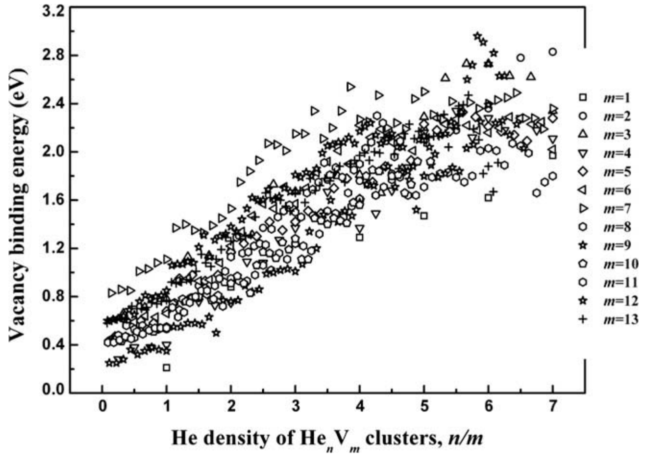

Fig. 5. The binding energy of a vacancy to He$_n$V$_m$ clusters as a function of the He density of the clusters.

energy required to bind the *n*th He atom in a He$_n$V$_m$ cluster. Notes that for the smaller ratio of *n*/*m*, the binding energy approximately equals to the formation energy of an interstitial He atom in Pu lattice (The interstitial He atom in Pu lattice is 2.3 eV by using our developed potentials.). It shows that He atom is most strongly bound to the large nearly empty voids, because He exists in a nearly free state. The high binding energies also explain the formation of He bubbles. The binding energy of an interstitial He atom to He$_n$V$_m$ clusters gradually decreases with increasing He density, followed by an increase at He density greater than 6. As illuminated by Morishita et al. [9], the change in the dependence of the energies on the He density at greater than 6 may be originated from the athermal SIAs production and associated effective decrease in the He density. In other words, the collective motion of He atoms in the cluster produces bubble pressure large enough to push the Pu atoms off from their normal lattice sites and spontaneously creates addition vacancies and SIAs, therefore increasing the bubble volume and thus lowering the He density. The process is more like the self-trapping mechanism of He bubble formation in the perfect crystal [15,16]. In fact, our present studies have shown that five He atoms clustering together in a perfect Pu lattice are sufficient to spontaneously push a Pu atom off from its normal site, thereby creating a Frenkel pair and a deeply-bound He cluster. The introduction of further He atoms produces more Frenkel pairs. The results indicate that the maximum *n*/*m* ratio in a He$_n$V$_m$ cluster is about 6. This athermal behavior may effectively increase the number of vacancies in the cluster, consequently, reduce the actual He density of the cluster.

The trend of SIA binding energy of to He$_n$V$_m$ clusters as a function of He density is similar to that of He binding energy. The binding energy of a SIA to He$_n$V$_m$ clusters also decreases with increasing He density, followed by an increase at He density greater than 6, which confirms that the athermal SIAs and vacancies are created at He density about 6. Fig. 5 shows the binding energy of a vacancy to He$_n$V$_m$ clusters as a function of He density. The binding energy of a vacancy to He$_n$V$_m$ clusters gradually increases with increasing He density, followed by a slowly decrease at high He density greater than 6, which is consistent with the He binding energy curve in Fig. 4, where the dependence of the binding energy on He density changes when the ratio is greater than 6. The calculated binding energy of a vacancy to the high-density He$_n$V$_m$ clusters surprisingly reaches 3.0 eV, suggesting that a vacancy in the He$_n$V$_m$ cluster energetically difficult to be detrapped from the clusters even at high temperature, especially in the cases of *n*/*m* greater than 4.

4. Conclusion

In this paper, the formation energies and binding energies of He$_n$V$_m$ clusters in Pu have been studied by using MD technique and the δ Pu MAEAM potential developed by our research group. The main results of these calculations are that the vacancy binding energy increases and the He and SIA binding energies decrease with the increase of the He density. All the binding energies mainly depend on the He–vacancy ratio of the clusters rather than the clusters size. Although the results are obtained from atomic scale, they already give glues in understanding the initial stage of He bubble nucleation and formation. From the results we can conclude that the He atoms can easily trapped at the vacancies which can act as nucleation centers for bubble formation. That is to say, He atoms can stabilize He$_n$V$_m$ clusters. The computational results may play an important role in understanding the initial formation and growth of He bubble in Pu.

Acknowledgements

This work was supported by the National Natural Science Foundation of China under contract number 20801007 and the Science and Technology Foundation of China Academy of Engineering Physics under contract number 20060542.

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