Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Journal of Nuclear Materials 350 (2006) 83–88
journal of nuclear materials
www.elsevier.com/locate/jnucmat

Atomistic behavior of helium–vacancy clusters in aluminum ☆

B.Y. Ao [a], J.Y. Yang [b], X.L. Wang [a], W.Y. Hu [b,*]

[a] *China Academy of Engineering Physics, P.O. Box 919-71, Mianyang 621900, Sichuan, People's Republic of China*
[b] *Department of Applied Physics, Hunan University, Changsha 410082, Hunan, People's Republic of China*

Received 3 November 2004; accepted 22 November 2005

Abstract

We have performed a molecular dynamics (MD) technique to calculate the formation energies of small He_nV_m clusters in Al using the embedded atom method (EAM), the Baskes–Melius potential and the Lennard-Jones potential for describing the interactions of Al–Al, Al–He and He–He, respectively. The binding energies of an interstitial He atom, an isolated vacancy and a self-interstitial Al 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. The binding energies of a He atom and an Al atom to a He_nV_m cluster decrease with the ratio, but the binding energy of a vacancy to a He_nV_m cluster increases with the ratio. The results indeed show that He atoms can increase the binding energy of a vacancy to a He_nV_m cluster, and decrease the binding energies of a He atom and an Al atom to the cluster, namely, He atom acts as a catalyst for the formation of He_nV_m clusters.

PACS: 97.10.Gz; 97.30.Qt; 97.80.Gm

1. Introduction

The behavior of He in metals is a topic of considerable current interest from both fundamental and technological points of view. Since He is inert and extremely insoluble in metals, it introduced into metals by implantation, or through nuclear reactions, or by tritium decay (sometimes calls tritium trick), or by alpha-decay in radioactive materials [1] has a strong tendency to precipitate and form bubbles with a high density of gas atoms. The presence of He in the matrix considerably modifies the properties of metals, which has been studied by many researchers [2]. It has been shown that clustering of He plays an important or even decisive role in the process that leads to intolerable modification of metals. Despite the many years of research regarding He effects with direct and indirect techniques in metals there are still many unknowns, specially regarding the initial stages of nucleation of such defects as bubbles and voids. As is well known, He bubble and void formation indeed is a quite complex phenomenon and involves several elementary mechanisms. So far, a physically precise description of bubble nucleation and the transformation of clusters into bubbles have not been studied systematically. In

---

☆ Supported by Science and Technology Funds of China Academy of Engineering Physics under Contract Number 20040546.

* Corresponding author. Tel.: +86 731 882 3971.
E-mail address: wangyuhu2001cn@yahoo.com.cn (W.Y. Hu).

0022-3115/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2005.11.014

terms of Trinkaus's [3] classification of He bubbles 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 bubbles. Although there are many atomistic studies on small He clusters in metals [4–7], the atomistic behaviors of He_nV_m clusters in metals have not been studied in detail by atomistic methods with few exceptions, among them the classical works of Adams and Wolfer [8], who studied formation energies of helium-void complexes in Ni. More recently, Morishita et al. [9–11] have investigated the growth and shrinkage behaviors of He_nV_m clusters in Fe by applying multiscale modeling approach which combines MD and kinetic Monte Carlo (KMC) techniques. They found that He atoms in a He_nV_m cluster can stabilize the cluster by suppressing vacancy emissions, and by promoting self-interstitial atom (SIA) emissions and the thermal emissions of a vacancy, an interstitial He atom and a SIA from He_nV_m clusters greatly depend on the He density of the clusters, rather than the clusters size.

In order to obtain further knowledge about the initial stages of He_nV_m cluster or He bubble nucleation in metals, the MD simulations are performed to investigate the behaviors of He_nV_m clusters. The purpose of this paper is to extend these calculations for the formation energies of He_nV_m clusters and investigate the role played by vacancies, SIAs and He atoms during bubble and void formation in metals. The behavior of He_nV_m cluster in Al is a special example. The paper is organized as follows. In Section 2, the methods and models used are briefly described which allow a pertinent description of the He–vacancy interaction in Al. The calculations are discussed in Section 3. Conclusive comments are provided in Section 4.

2. Computational methods

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 Al atoms, a potential based on the EAM is used [12,13]. EAM is a popular and effective approach for modelling 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 when very many time steps would be required in a dynamic simulation. The interaction potential for He–He is the Lennard-Jones potential which has been widely used to study the He effects in metals. He–Al potential is obtained by fitting the free-electron He–Al pair potential [14]. The formation energy of a He_nV_m cluster that contains n He atoms and m vacancies are defined as follows:

$$E_f(He_nV_m) = E_{tot}(He_nV_m) - n\varepsilon_{He} - (N-m)\varepsilon_{Al}, \tag{1}$$

where $E_f(He_nV_m)$ is the formation energy of He_nV_m cluster with n He atoms in a void of m vacancies, $E_{tot}(He_nV_m)$ is the calculated total energy of a computational cell containing a He_nV_m cluster, ε_{Al} is the cohesive energy of a perfect fcc Al crystal, and ε_{He} is the cohesive energy of a perfect fcc He crystal. Here, the calculated cohesive energies of perfect crystals are -3.39 eV/atom and -0.0071 eV/atom for Al and He, respectively. N denotes the number of perfect fcc lattice sites in the computational cell and therefore $(N-m)$ is the number of Al atoms in the cell. Especially, if $n = 0$, namely, there is no He atom in the cluster, the formation energy of the void containing m vacancies (V_m) is defined as follows:

$$E_f(V_m) = E_{tot}(V_m) - (N-m)\varepsilon_{Al}. \tag{2}$$

The solubility of He in Al is described by the binding energies of a vacancy $E_B(V)$, a He atom $E_B(He)$ and a SIA $E_B(SIA)$ to a He_nV_m cluster, which are calculated from the following equations:

$$E_B(V) = E_f(He_nV_{m-1}) + E_f(V) - E_f(He_nV_m), \tag{3}$$

$$E_B(He) = E_f(He_{n-1}V_m) + E_f(He) - E_f(He_nV_m), \tag{4}$$

$$E_B(SIA) = E_f(He_nV_{m+1}) + E_f(SIA) - E_f(He_nV_m). \tag{5}$$

$E_f(V)$ is the single vacancy formation energy. $E_f(He)$ is the formation energy of He in an interstitial site and $E_f(SIA)$ is the SIA formation energy. Similarly, if $n = 0$, namely, there is no He atom in the cluster, the binding energy of a vacancy to the void containing m vacancies is defined as follows:

$$E_B(V) = E_f(V_{m-1}) + E_f(V) - E_f(V_m). \tag{6}$$

The defects formation energy is determined by comparing the energy of a crystal containing defects with a crystal of the same number of atoms on their perfect lattice sites. Three-dimensional periodic cell of $10a_0 \times 10a_0 \times 10a_0$ is used, where a_0 is the lattice constant. 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 di-vacancy 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 [15], followed by slowly cooling and quenching the system to 0 K [16]. 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.

3. Results and discussion

3.1. Self-trapping of helium

When defects are not introduced, as is the case with low-energy helium implantation or with helium-3 introduction through tritium trick, the He atoms can cluster and form bubble by self-trapping model [17–19]. In the present calculation, we begin with the configuration for one He atom at the interstitial site of the perfect fcc Al lattice, and then try placing additional He atoms in various positions until the configuration having lowest formation energy is found. Afterwards, MD simulation is performed. Generally speaking, we consider the Al atom that the displacement distance from its normal site exceeds the radius ($r_{Al} = 1.43$ Å) of Al atom as a displaced atom, i.e. a SIA. During the course of MD simulation, we find that the collective action of even small clusters of He atoms is sufficient to spontaneously create additional vacancies and associated SIAs. That is, the He atom can push Al atoms off their normal lattice sites. These lattice atoms, however, energetically prefer to remain in the near vicinity of the cluster resulting in a near-Frenkel-pair defect. Most importantly, SIA stabilization provides a mechanism for bubble growth without requiring the SIA to detrap.

It is obviously that the calculation time is very expensive when all kinds of possible configurations are taken into account, especially for the case of many He atoms. So only several computational cells are selected for the MD calculation, and the He atoms are closely located at the tetrahedral interstitial sites if the number of He atoms exceeds 16. Present calculated results indicate that five He atoms cluster together in a perfect Al lattice is sufficient to spontaneously push an Al 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: Eight He atoms create the second and the third such defects, and with 16 He atoms as many as 5 Frenkel pairs can be produced, and with 48 He atoms more than 20 Frenkel pairs can be produced. Notable is the fact that the SIAs themselves cluster together forming interstitial loop. These results are in reasonably good agreement with previous studies [17–19], which indicates that the present calculated method and interatomic potentials are accurate.

3.2. 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 configuration. Clearly, the vacancy type defect such as empty void should be a likely place for He atom to fill. Using the simulation approach 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 Al. As shown in the figure, the total formation energies of voids increase with the number of vacancies in them. There are some maximums in the plot of vacancy binding energy versus the number of vacancies, from which we can include 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 to fill. However, even for the larger size of voids,

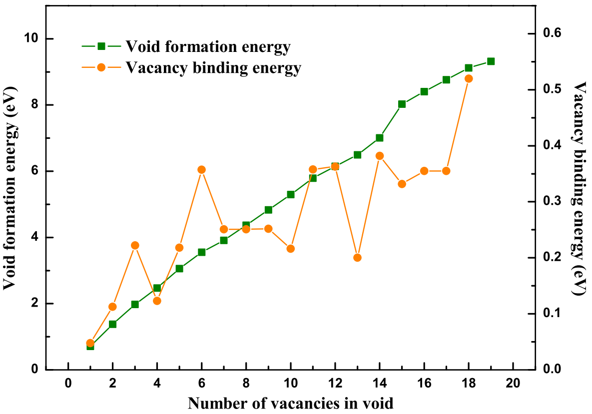

Fig. 1. Void formation energy and vacancy binding energy as a function of the number of vacancies.

the vacancy binding energy does not exceed 0.6 eV. The vacancy binding energy is dramatically changed when He atoms are introduced into the voids, as mention in the following discussion, the maximal vacancy binding energy is about 3.5 eV.

3.3. Formation energies of He_nV_m clusters

The formation energies of He_nV_m clusters are the foundation of calculating the defect binding energy. Fig. 2 shows the formation energies of He_nV_m clusters are in dependence on number of He atoms. It can be seen that for He in Al, the formation energies of He_nV_m clusters slowly increase with the introducing of He until the He to vacancy ratio is greater than 1, which indicates the lowest energy configuration occurs when there is one vacancy per He atom.

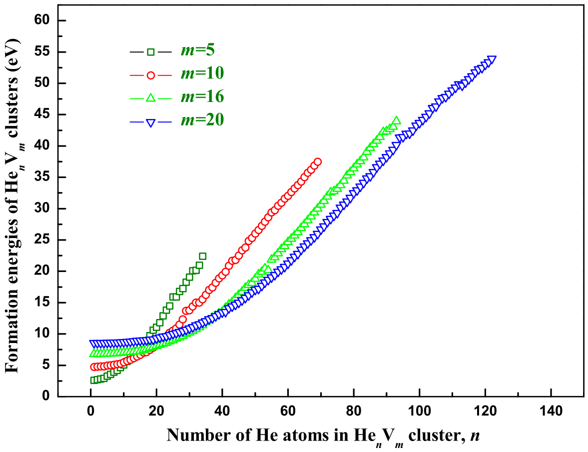

Fig. 2. He_nV_m formation energy as a function of the number of the He atoms.

3.4. Binding energies of a He atom, an Al atom and a vacancy to He_nV_m clusters

According to the Eqs. (3)–(5) the binding energies of a He atom, an Al atom and a vacancy to a He_nV_m cluster have been calculated. These binding energies are graphed in Figs. 3–5, respectively. The He density is defined as the He to vacancy ratio of the He_nV_m cluster, which is the number of He atoms divided by the number of vacancies in the cluster. Namely, the He density of a He_nV_m cluster provided by n/m. As shown in the three figures, the binding energies show a strong dependence on the He density.

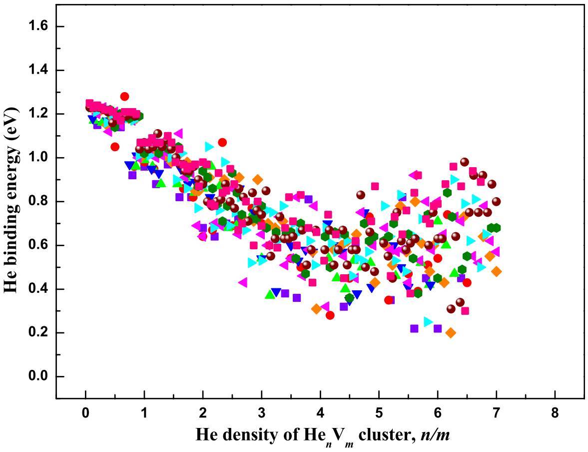

Fig. 3. The binding energy of a He atom to He_nV_m cluster as a function of the He density of clusters.

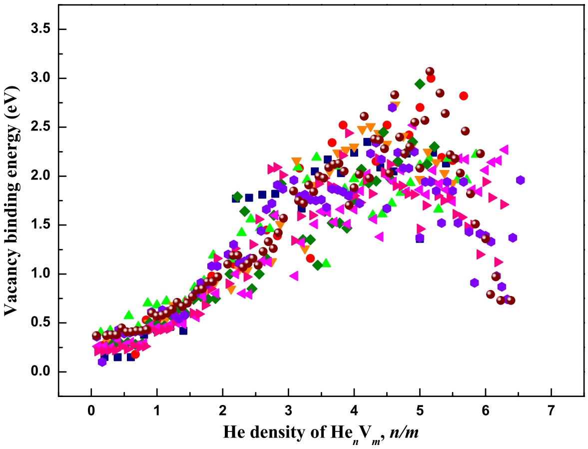

Fig. 4. The binding energy of a vacancy to He_nV_m cluster as a function of the He density of clusters.

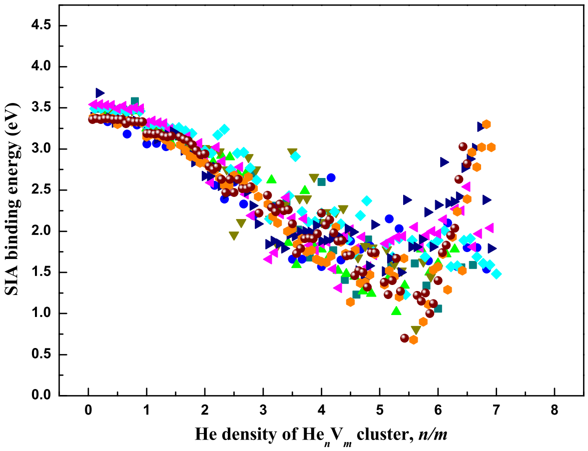

Fig. 5. The binding energy of an Al atom to He$_n$V$_m$ cluster as a function of the He density of clusters.

The He binding energy represents the energy required to bind the *n*th He atom in a He$_n$V$_m$ cluster. Notes that for the small ratio of He/V the binding energy approximately equals to the formation energy of interstitial He (the energy is 1.25 eV). It shows that He 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 5 He/V. As illuminated by Morishita et al. [9–11], the change in the dependence of the energies on the He density at greater than 5 He/V may be because of 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 Al 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 results indicate that the maximum He/V ratio is about 5. This athermal behavior may effectively increase the number of vacancies in the cluster, consequently, reduce the actual He density of the cluster.

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 5 He/V, 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 5. The calculated binding energy of a vacancy to the high-density He$_n$V$_m$ clusters surprisingly reaches 3.5 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 3.

Fig. 5 also shows the binding energy of a SIA to He$_n$V$_m$ clusters as a function of He density. Similar to the density dependence of the He binding energy, the binding energy of a SIA to He$_n$V$_m$ clusters also decreases with the increasing He density, followed by an increase at He density greater than 5 He/V, which reconfirms that the athermal SIAs and vacancies are created at He density about 5 He/V.

4. Conclusion

In this paper, the formation energies and the binding energies of He$_n$V$_m$ clusters in Al have been calculated by using MD technique. The main results of these calculations are that the vacancy binding energy increases with the He density, but the He and SIA binding energies decrease with 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 stages 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.

Acknowledgements

This work was supported by Science and Technology Funds of China Academy of Engineering Physics under contract number 20040546. One of the authors (B.Y. Ao) thanks Dr Li Huang for his help in preparing this paper.

References

[1] M.S. El-Genk, J.M. Tournier, J. Nucl. Mater. 280 (2000) 1.
[2] H. Trinkaus, B.N. Singh, J. Nucl. Mater. 323 (2003) 229.
[3] H. Trinkaus, Radiat. Eff. 78 (1983) 189.
[4] K.O. Jensen, R.M. Nieminen, Phys. Rev. B 36 (1987) 8219.
[5] J.M. Cayphas, M. Hou, L. Coheur, J. Nucl. Mater. 246 (1997) 171.
[6] E.M. Bringa, B.D. Wirth, M.J. Caturla, J. Stölken, D. Kalantar, Nucl. Instrum. and Meth. B 202 (2003) 56.

[7] M.J. Caturla, T.D. de la Rubia, M. Fluss, J. Nucl. Mater. 323 (2003) 163.
[8] J.B. Adams, W.G. Wolfer, J. Nucl. Mater. 166 (1989) 235.
[9] K. Morishita, R. Sugano, B.D. Wirth, J. Nucl. Mater. 323 (2003) 243.
[10] K. Morishita, R. Sugano, B.D. Wirth, T.D. de la Rubia, Nucl. Instrum. and Meth. B 202 (2003) 76.
[11] K. Morishita, R. Sugano, B.D. Wirth, Fus. Sci. Technol. 44 (2003) 441.
[12] M.S. Daw, S.M. Foiles, M.I. Baskes, Mater. Sci. Rep. 9 (1993) 251.
[13] W.Y. Hu, H.Q. Deng, X.J. Yuan, M. Fukumoto, Euro. Phys. J. B 34 (2003) 429.
[14] M.I. Baskes, C.F. Melius, Phys. Rev. B 20 (1979) 3197.
[15] M. Parrinello, A. Rahman, Phys. Rev. Lett. 45 (1980) 1196.
[16] M.P. Allen, D.J. Tildesley, Computer Simulation of Liquids, Oxford University, New York, 1987.
[17] W.D. Wilson, M.I. Baskes, C.L. Bilson, Phys. Rev. B 13 (1976) 2470.
[18] W.D. Wilson, C.L. Bilson, M.I. Baskes, Phys. Rev. B 24 (1981) 5616.
[19] W.D. Wilson, Radiat. Eff. 78 (1983) 11.