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Molecular Dynamics Simulations of Helium Behaviour in Titanium Crystals *

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Molecular dynamics simulations are performed to investigate the behaviour of helium atoms in titanium at a temperature of 300 K. The nucleation and growth of helium bubble has been simulated up to 50 helium atoms. The approach to simulate the bubble growth is to add helium atoms one by one to the bubble and let the system evolve. The titanium cohesion is based on the tight binding scheme derived from the embedded atom method, and the helium–titanium interaction is characterized by fitted potential in the form of a Lennard-Jones function. The pressure in small helium bubbles is approximately calculated. The simulation results show that the pressure will decrease with the increasing bubble size, while increase with the increasing helium atoms. An analytic function about the quantitative relationship of the pressure with the bubble size and number of helium atoms is also fitted.

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Titanium, a useful material to store and retrieve hydrogen, has many important technological applications. Hydrogen and its isotopes are insoluble in hexagonal α-titanium at room temperature. As a consequence of tritium decay, titanium containing tritium becomes doped with ^{3}He, which gradually agglomerate into bubbles that deteriorate material properties. Thus the behaviour of helium in titanium has attracted considerable interest in recent years. During the past several decades, both experimental and theoretical investigations on the behaviour of helium in metals have increased.[1−5] However, the fundamental understanding of the microscopic behaviour of helium in materials is still incomplete. The helium in metals forms tiny, high-pressurized bubbles at room temperature,[6] the bubble growth occurs by random bubble migration and coalescence. In certain helium embrittlement theories, over-pressurization of grain boundary cavities is thought of as the key factor leading to the weakening of the materials.[7] The technological interest in the estimate of the relative pressure of helium in bubbles arises too.

The molecular dynamics (MD) method has been extensively used to study the behaviour of atoms.[8−11] Although it is not expected to be as accurate as the *ab initio* method, MD is a convenient way to handle the atomic system at the atomic scale, particularly in modelling of large systems which contain thousands of atoms. In this Letter, the growing process of helium bubbles containing 50 helium atoms is simulated by the MD method. The pressure of helium bubbles, which contributes to a better understanding of the behaviour of helium atoms, is investigated in the evolution. A fitted formula of pressure of helium bubbles is obtained in good agreement with the calculated results.

The simulation is performed in a NVT system with temperature 300 K. An electron–phonon coupling model is adopted to control the temperature of the system.[12] For the He–Ti system, a rectangular parallelepiped box (the box scale is $15a_0 \times 15a_0 \times 15a_0$, where a_0 is the lattice constant of Ti, $a_0 = 2.951$ Å) is constructed. The number of titanium atoms is 6480. The periodic boundary conditions are applied in all three dimensions to represent the macroscopic system more closely. The initial velocities of titanium atoms are assigned at random but distributed to conform to Maxwell–Boltzmann distribution at 300 K.

The major parameter which governs the dynamics of atomic interactions is the potential from which the interatomic forces derive. The embedded atom method (EAM) developed by Daw and Baskes[13,14] has been successfully applied to study atomic interactions in metals and intermetallic alloys. In the case of titanium, the tight-binding potential, a relatively simple EAM potential, is used in a titanium matrix to describe the interaction between titanium atoms.[15] The potential energy may be written as

$$E_{\rm tot} = \sum_i (E_R^i + E_B^i), \tag{1}$$

with

$$E_R^i = \sum_j A_{\alpha\beta} e^{-p_{\alpha\beta}(r_{ij}/r_0^{\alpha\beta}-1)}, \tag{2}$$

$$E_B^i = -\Big[\sum_j \xi_{\alpha\beta}^2 e^{-2q_{\alpha\beta}(r_{ij}/r_0^{\alpha\beta}-1)}\Big]^{1/2}. \tag{3}$$

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The interatomic Ti–Ti potential consists of two contributions, namely, the effective band term E_B^i plus a short-range repulsive pair potential E_R^i. In Eqs. (2) and (3), the parameter values $A = 0.1519\,\text{eV}$, $p = 8.620$, $r_0 = 2.951\,\text{Å}$, $\xi = 1.8112\,\text{eV}$ and $q = 2.390$, respectively.

The major requirement for the He–Ti interaction is that it yields the correct potential for the helium atom near the titanium atoms, when contributions from all metal atoms added for each helium atom. As there is no potential to give a good description of He–Ti interaction, the pairwise potential in the form of Lennard–Jones function, given by Eq. (4), is used for the He–Ti interaction. The He–Ti potential [16] can be expressed as

$$V(r) = \varepsilon\Big[\Big(\frac{r_0}{r}\Big)^{4.35} - 3.21\Big(\frac{r_0}{r}\Big)^{1.4}\Big], \tag{4}$$

where $\varepsilon = 0.02617\,\text{eV}$, $r_0 = 4.7288\,\text{Å}$. The parameters of the Lennard-Jones function are determined on the basis of a genetic algorithm using data from ab initio calculations.

Finally, the He-He interaction is described by HFDHE2.[17] This potential gives somewhat good results compared to other potential, in the form

$$V(r) = \varepsilon V^*(x), \tag{5}$$

where

$$V^*(x) = A\exp(-\alpha x) - \Big\{\frac{C_6}{x^6} + \frac{C_8}{x^8} + \frac{C_{10}}{x^{10}}\Big\}F(x), \tag{6}$$

$$F(x) = \begin{cases} \exp[-(D/x-1)^2], & \text{for} \quad x < D, \\ 1, & \text{for} \quad x \geq D, \end{cases} \tag{7}$$

where $x = r/r_m$, and all the other parameters such as D and α have been given in Ref. [17].

In the present simulation, the initial configuration of the system is the perfect *hcp* Ti lattice without defects introduced. The first helium atom is randomly introduced to the system, followed by evolution for 50 ps, and the second one is added to the system about one lattice distance away from the first one. As the system reaches thermodynamic equilibrium, a helium dimer is formed in accompany with a Ti atom ejected to be a self-interstitial atom. The dimer acts as a trapping site to trap subsequent helium atoms randomly travelling in its neighbouring region. Thus the bubble growth is performed via the sequential addition of helium atoms to the system about one lattice distance away from the closest atom in the cluster to reduce the simulation time. In the course of simulation, the collective action of even small clusters of helium atoms is sufficient to spontaneously create additional vacancies and associated self-interstitials. The self-interstitials induced by helium cluster has a tendency to congregate on one side of the cluster as shown in Ref. [16]. The simulations of bubble growth are carried out till the number of helium atoms reaches 50. For the statistical reason, the same simulation is repeated for five times with different initial configurations. Figure 1 shows an example of bubble growth result including 50 helium atoms.

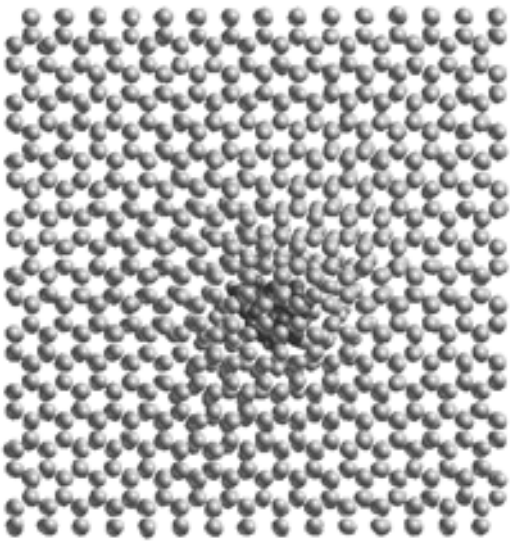

Fig. 1. Configuration of a titanium crystal containing 50 helium atoms. The black and grey balls denote helium and titanium atoms, respectively.

The pressure of helium bubbles is investigated to a better understanding of the behaviour of helium atoms in titanium. As the behaviour of helium in the substrate material is far from that of an ideal gas and the pressure in small helium bubbles may be extremely high, the concept of an ideal gas is entirely inappropriate. The bubble pressure may be calculated via the improved equation of state (seen Ref. [18]):

$$p = \rho k_B T + \varpi/V, \tag{8}$$

where p is the pressure, ρ is the density, k_B is Boltzmann's constant, T is temperature, V is the volume and ϖ is the internal virial written as

$$\varpi = \frac{1}{3}\sum_{i=1}^{N} \boldsymbol{r}_i \cdot \boldsymbol{f}_i, \tag{9}$$

where $\boldsymbol{r}_i$ is position of the ith atom and $\boldsymbol{f}_i$ is the force on this atom.

For the present application, the corresponding pressure p is determined according to Eq. (8). The pressures of the helium bubbles containing 10, 20, 30, 40 and 50 atoms are computed, respectively. For comparison, the pressure of the substrate material is also calculated. As shape of the bubble is irregular, it is difficult to determine actual volume of the bubble. As shown in Fig. 2, we define the pressure of helium bubble as the pressure of an approximately spherical re-

gion of radius r that contains all helium atoms and some neighbouring metal atoms.

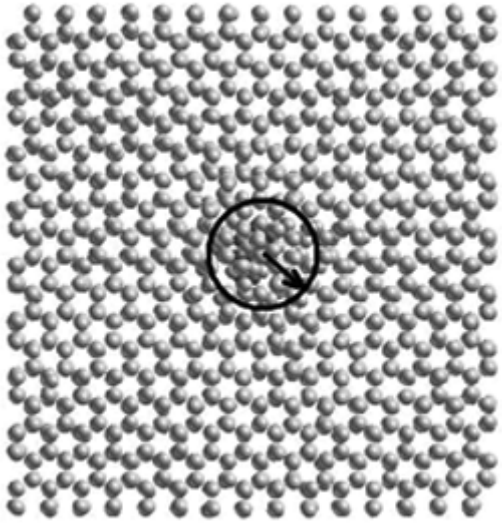

Fig. 2. Scheme indicating the method of defining the pressure caused by the helium bubble. The helium bubble is considered as a spherical structure. The pressure in an approximately spherical region of radius r is calculated.

The simulations of helium bubble growth are performed at the constant temperature 300 K. The calculated results show that the pressure fluctuates on time due to thermal vibration of the atoms. The fluctuation will decrease with the increasing radius of the spherical region. Figure 3 presents a plot of the pressure as a function of the simulated time for the bubble containing 50 helium atoms. Note that statistical square error of the computed pressure is approximately 20 kbar for $r = 1a_0$ with a_0 being the lattice unit, the value is 3.4 kbar for $r = 2a_0$. For $r = 5a_0$, the value is about 1 kbar. When $r \geq 2a_0$, statistical square error is less than 5 kbar and all 50 helium atoms can be included in the spherical region, so the data of the bubble pressures for $r < 2a_0$ are not adopted for fitting formula of pressure of helium bubbles. Considering that the growth of helium bubble is a random process and the different initial simulation configurations could result in different helium bubble configurations and thus different pressure. The helium bubble pressure should be averaged on these configurations. As an example, Fig. 4 shows three configurations of helium bubble containing 50 helium atoms (the radius of the spherical region $r = 2a_0$) that are resulted from different initial configurations. The corresponding average pressures over 5ps time steps are 49.33, 42.54 and 52.02 kbar, respectively. Thus, we refer the helium bubble pressure to the statistical average on relaxation time and configurations. In the present study, for given helium bubble size, the pressure is the average on five simulation results with different initial configurations. Figure 5 shows the relationship between the pressure and the size of the spherical region. By fitting these results, this relationship could be described by an analytic function as follows:

$$p = \frac{1}{r} 59.05 e^{-0.19r} (n + 3.08)^{0.36} - 36.4, \qquad (10)$$

where p is the bubble pressure in kbar, r is the radius defined in Fig. 2 and n is the number of helium atoms in the bubble. As shown in Fig. 5, the results calculated by Eq. (10) are in good agreement with the computed pressures.

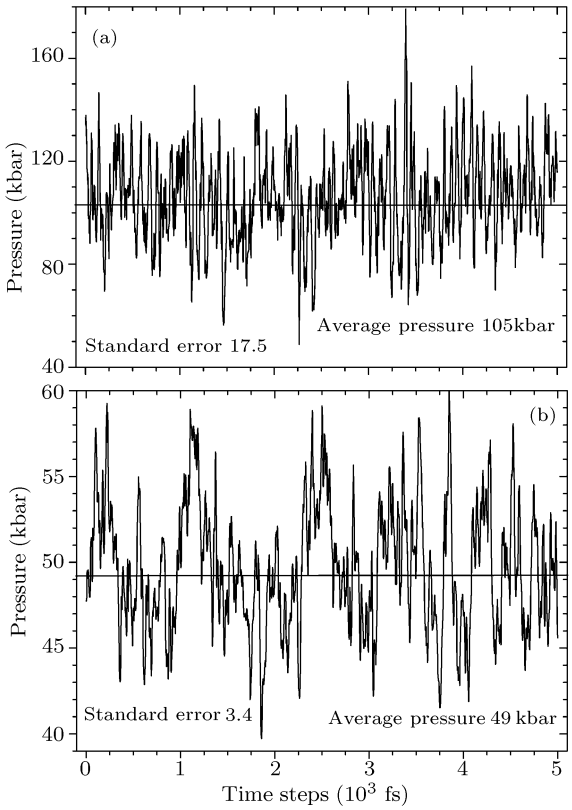

Fig. 3. Time dependence of the pressure for (a) $r = 1a_0$ (the radius of the spherical region) (b) $r = 2a_0$ with a_0 being the lattice unit.

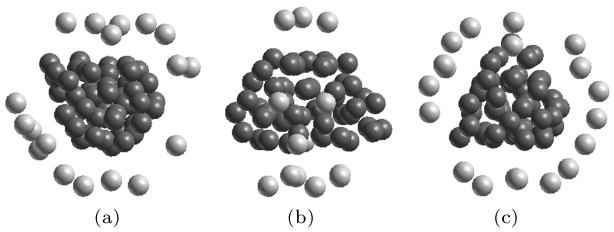

Fig. 4. Three configurations of helium bubble containing 50 helium atoms, due to the different initial configurations (the radius of the spherical region $r = 2a_0$), for average pressures (a) 49.33 kbar, (b) 42.54 kbar, (c) 52.02 kbar.

The simulation method, suitable to describe the behaviour of helium in titanium substrate, is estab-

lished. As is shown in Fig. 5, the preliminary conclusion presents that the bubble pressure gradually decreases with the increasing size of the spherical region. Initially, when the radii of the spherical region are in the range of $1a_0 - 4a_0$, the bubble pressure sharply drops with the increasing radii of the spherical region. When the radius changes from $4a_0$ to $5a_0$, it is found that there is a slight reduction in pressure of the helium bubble. The bubble pressure has a tendency to increase with the increasing helium atoms.

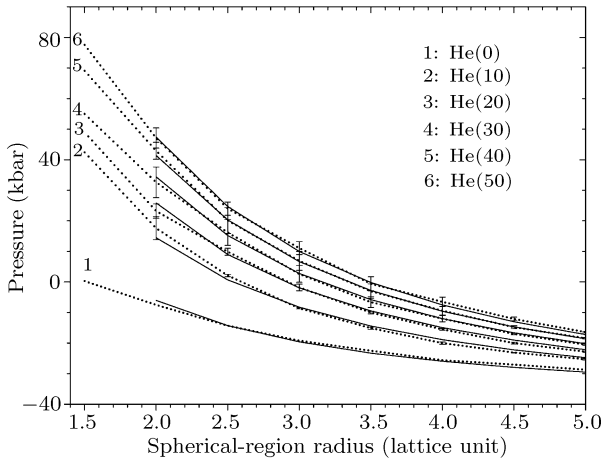

Fig. 5. Computed pressure of the spherical region containing the different number of helium atoms as a function of the radius of the spherical region. The solid curve is a fit to the data.

So far, a great number of cases have been reported in the literature on the pressure formulas of helium bubble.[19] However, in most of these cases, the helium bubble was considered as a spherical structure. In our simulation, helium atoms are introduced one by one, the helium bubble and the defect are not symmetrical at little size in agreement with the simulation results from other researchers.[1,20] Therefore, in the calculation of the helium bubble in this study, the spherical region of radius r includes both helium atoms and metal atoms due to the difficulty of defining the volume of the helium bubble. We have also tried to fit the calculated results by employing a simple form $(p = 2\gamma/r)$ from the literature,[19] whereas the result is unsatisfactory. It must be mentioned again that our pressure formula is obtained at a bubble size not more than 50 helium atoms and applicable to the early formation stage of helium bubble.

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