Journal of Nuclear Materials 455 (2014) 258–262

Contents lists available at ScienceDirect

Journal of Nuclear Materials

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

An atomistic assessment of helium behavior in iron ☆

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ARTICLE INFO

Article history:
Available online 22 June 2014

ABSTRACT

High helium generation rates in irradiated materials leads to the formation of small He–vacancy clusters that can evolve into larger bubbles and voids. An equation of state that accurately reproduces their pressure–volume relationship is necessary to understand and predict the behaviour of these He–vacancy defects. Previous research has employed equations of state of varying complexity, including the ideal gas, van der Waals, and hard sphere models. We recently used ab initio calculations to determine the energetics of helium-vacancy clusters and applied the results to develop a new three-body interatomic potential that describes the behaviour of helium in iron. This potential was employed in molecular dynamics simulations to determine the conditions for mechanical equilibrium between small helium-stabilized bubbles and an iron matrix, and to systematically map the pressure–volume relationship for the bubbles at a range of temperatures. These atomistic results are compared to an existing equation of state and a modification is proposed for bubbles with high helium densities.

1. Introduction

Helium is produced in irradiated metals and alloys by (n, α) transmutation reactions, and strongly influences microstructural and mechanical property changes. Helium effects are a particular concern for DT fusion reactor conditions because this environment will lead to significantly higher levels of He production than in fission reactor irradiation experiments where most data on radiation effects has been obtained. A prominent result of high He levels is the formation of very high densities of small He–vacancy clusters that can evolve into larger bubbles and voids. A computational model capable of predicting the behaviour of these small cavities requires an accurate equation of state to reproduce the pressure–volume relationship. Previous research has employed equations of state of varying complexity, including the ideal gas, van der Waals, and hard sphere models. Recent advances in high performance computing have made it possible to employ *ab initio* calculations to determine the energetics of larger and more complex atomic systems. Such calculations were used as the basis for development of a new three-body interatomic potential that accurately describes the behaviour of helium as either a substitutional or interstitial impurity in iron [1,2]. Molecular dynamics simulations employing this potential have been used to determine the conditions for mechanical equilibrium between small helium-stabilized bubbles and the iron matrix, and to systematically map the pressure–temperature relationship for He-filled bubbles. These atomistic results build on our previous research [3,4], and are compared to a hard-sphere equation of state we have used previously [5,6]. A modification of the hard-sphere model is proposed for bubbles with high helium densities.

2. Simulation method

Molecular dynamics (MD) simulations were carried out at constant volume using a bcc iron system size of 128,000 iron atoms (40 lattice parameters cubed) containing helium-filled bubbles consisting of 9 to 44,399 vacancies, corresponding to nominal radii (r_b) from ~0.25 nm to ~5.0 nm. The appropriate lattice parameter was used for each simulation temperature in the range from 300 to 1000 K. The helium density in the bubbles was the primary simulation variable, with the density expressed as either the helium-to-vacancy ratio or the number of helium atoms per unit volume. Note that when the bubble volume is required, it is calculated based on the number of vacancies in the bubble and the atomic volume, i.e. $V_b = n_v\Omega$, and not as a sphere of radius r_b. This distinction is particularly important for small bubbles. The interatomic potentials employed were those of Ackland and co-workers for iron [7] and the ORNL three-body He–Fe potential [2]. For each simulation condition, the simulations were carried out long enough (see

☆ Research sponsored by the Office of Fusion Energy Sciences, U.S. Department of Energy, under contract DE-AC05-00OR22725 with UT-Battelle, LLC. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes.

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http://dx.doi.org/10.1016/j.jnucmat.2014.06.020
0022-3115/

below) to obtain an accurate determination of the bubble pressure. There is a slight linguistic ambiguity in the following discussion. When carrying out MD simulations, it is common to use the term "equilibration" to describe the process of carrying out a simulation long enough for the total system energy to be equally distributed between kinetic and potential energy. We follow this convention here. However, we also wish to determine the equilibrium state of bubbles as discussed in the next paragraph. The latter we refer to as a condition of mechanical equilibrium. Although the MD simulations do not account for any influence of quantum effects that may occur with He at high densities, previous work indicated that these effects are not significant above about 50 K even for very high pressures [8].

He-filled bubbles, especially those with a small number of He-atoms, are not very convenient objects from a statistical point of view. In fact, it is difficult to accurately determine the pressure when a bubble contains relatively few gas atoms so that the frequency of atomic collisions is low. For such objects, the definition of equilibrium pressure becomes an even larger problem. The equilibrium condition is an important state for bubbles since at this point they are essentially a neutral object in the matrix. Several properties can be used to infer the degree of bubble equilibrium. For example, one could choose an energy criterion in which the bubble has equal probabilities of absorbing and emitting vacancies (and interstitial atoms in an irradiation environment) and therefore it is neither growing nor shrinking. In this research, we adopt a mechanical bubble dilatation criterion in which the equilibrium bubble does not produce any stress fields in the matrix. This is equivalent to a zero dilatation. In the context of our molecular dynamics simulations, this is determined in the following way. The lattice parameter corresponding to zero total pressure in perfect Fe is determined for a given temperature, and a void of radius r_b having N_v vacancies is created in the crystal with this lattice parameter. An initial number of He-atoms m_{He} is inserted into the void. The whole system is annealed at the target temperature until the He-atoms inside the bubble are in complete equilibrium with Fe matrix. The equilibration time is strongly dependent on the void size and He-to-vacancy ratio. After equilibration, the matrix pressure is calculated from both the forces between the atoms and their velocities.

If a bubble is in mechanical equilibrium, the total average pressure in the matrix should be zero, determining the equilibrium number of gas atoms and pressure for a given bubble at a given temperature. Since we are interested in finding the equilibrium bubble, i.e. zero dilatation state, high accuracy can be obtained with a modest system size. We initiated the calculations with the bubble He content well below the estimated equilibrium value and determined the pressure. Then, the helium content was incrementally increased and the system equilibrated at the new helium density. This continued until the condition of mechanical equilibrium was reached with an accuracy of ~1%. Because mass of a He atom is very small, a time step of 0.2 fs was used in the MD integration. This very short time step, coupled with the long simulation times required to obtain a good statistical measure of the pressure (many atom collisions), led to a large number of MD steps in the simulations. Obtaining typical results required many millions of integration steps. The physical time simulated for each specific set of parameters varied from 1 ns for large bubbles (1.0–5.0 nm) to 2 ns for smaller bubbles (0.25–0.5 nm).

3. Results

The MD simulations which have been completed provide a sufficient basis to determine the desired pressure–volume–temperature relationship for small He bubbles in iron. Typical results showing the time required for the matrix pressure and the helium bubble pressure to reach equilibrium are shown in Figs. 1 and 2 at temperatures of 300 and 1000 K, respectively. Note that the required simulation time is longer and the bubble pressure fluctuations are larger for smaller bubbles and lower temperatures, both of which lead to fewer atom collisions per unit time. Conversely, the matrix pressure saturates more quickly for the smaller bubbles since they have less of a mechanical impact on the matrix. The results demonstrate the importance of using relatively long simulation times, and indicate that pressure fluctuations may limit the accuracy obtained for the smallest bubbles.

The calculated bubble pressures obtained from the MD simulations for equilibrium bubbles are shown in Fig. 3 as a function of the nominal radius. Multiple data points for each radius refer to different temperatures, which indicate a slight increase in pressure as the temperature decreases. The pressure is compared to that predicted by the so-called capillarity model, i.e. $P = 2. \cdot \gamma / r_b$, where γ is the surface energy [9]. Note that there is no explicit temperature dependence in the capillarity model, although it can be incorporated via the temperature dependence of the surface energy. The curve in Fig. 3 uses the average value of the surface energy obtained from MD simulations with the iron interatomic potential for a 2 nm void between 300 and 1000 K, 1.75 J/m^2. This is somewhat lower than the value of 1.82 J/m^2 which was obtained previously in static simulations [10]. There is quite reasonable agreement between the capillarity model and the equilibrium pressure except for the smallest 0.25 nm bubbles.

The helium density is a useful parameter for determining the helium inventory in irradiated materials, and is a critical parameter in any equation of state. The helium-to-vacancy ratio for equilibrium bubbles is shown in Fig. 4. The temperature dependence in

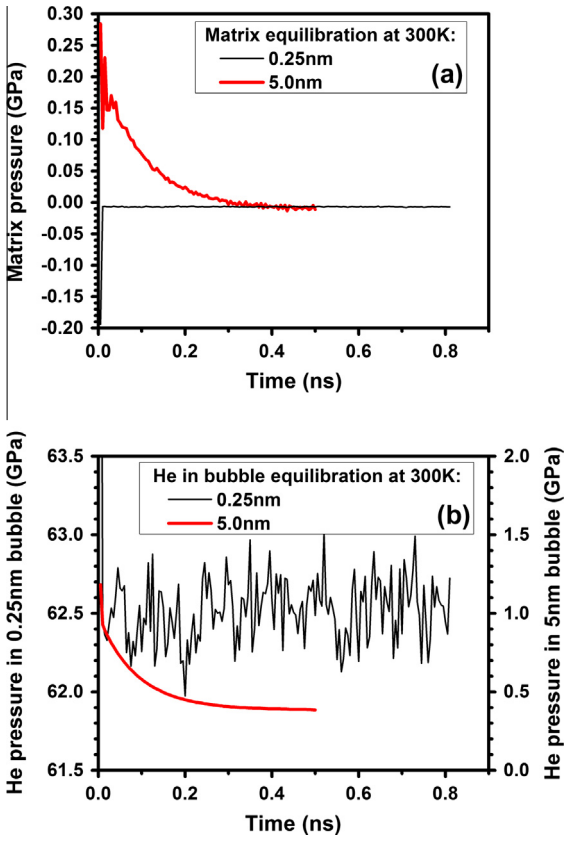

Fig. 1. Typical matrix (a) and bubble (b) equilibration times at 300 K for bubbles with radii of 0.25 and 5.0 nm.