8.4 MOLECULAR DYNAMICS INVESTIGATION OF HELIUM BUBBLE EQUATION OF STATE — Y. N. Osetskiy and R. E. Stoller (Oak Ridge National Laboratory)

OBJECTIVE

The objective of this research is to determine the equation of state of helium in radiation-induced bubbles in iron-based alloys. Properties of He-bubbles significantly affect the evolution of the microstructure and mechanical properties under radiation damage conditions.

SUMMARY

An extensive modeling program was launched earlier to model He-filled bubbles in Fe. We are studying bubbles of radius from 0.25 to 5.0nm with He-to-vacancy ratio from 0.1 to 2.0 over the temperature range 300-1000K. An unexpectedly long simulation time was found to be necessary to accurately determine the equilibrium properties of small bubbles.

PROGRESS AND STATUS

Introduction

An extensive simulation program using molecular dynamics (MD) is in progress to characterize the behavior of helium in small bubbles in iron as representative of Fe-based alloys. The objective is to obtain an accurate, atomistic-based equation of state, which describes the pressure-volume relationship for He in such bubbles as a function of temperature. This information is absolutely necessary for predicting radiation damage evolution in fusion materials where He is generated due to transmutation reactions. The presence of He strongly influences the microstructural processes controlling the formation and evolution of cavities, which in turn can that dramatically change the defect balance and kinetics of microstructural evolution.

Progress

The three-body, angular dependent interatomic potential for Fe-He developed earlier at ORNL [1,2] was used in this study. A special study was made to define the equilibrium state of gas-filled bubbles. We first used the concept of the bubble volume that was defined via the displacement of the surface atoms [3,4]. The general idea is that an equilibrium bubble should not induce additional displacements of the surface atoms, which should be in the same positions as if they were in a perfect lattice. This works well for nearly flat surfaces (large radii) and high concentrations of gas atoms, which permit one to accumulate high statistics of gas-surface interactions over a suitable averaging time. However, we found that this does not work well even for medium size bubbles, < 3-4 nm, because their surface is quite curved and the equilibrium He concentration is relatively low, a He-to-vacancy ratio of 0.25 to 0.5 depending on the temperature. This introduces a significant inaccuracy in definition of the equilibrium state. We then adopted another criterion, which is based on the average pressure in the Fe matrix. Formally, this definition is completely equivalent to the previous one; we define a bubble to be in equilibrium if it does not changes its original volume as defined in reference to the perfect lattice and therefore does not produce an additional pressure contribution in the Fe the matrix. Calculation of the total pressure in the system is fast and the average value converges well because of the large number of atoms used in practical modeling.

Another problem arises in a study such as this related to small bubbles, <0.5nm, due to inaccuracy of the statistical definition of thermodynamic parameters such as gas temperature and pressure in small systems. The smallest bubble we studied may contain as few as only one He atom and estimation of He temperature inside such a bubble becomes indeterminate. A similar but easier to resolve problem also arises for larger bubbles at the lowest temperatures. For example, at 300K the few slowly moving He atoms in bubbles 0.25-0.5nm have too few collisions with the bubble wall per unit time to define pressure easily. A bubble with a 0.25nm radius occupies only 9 lattice sites and with the equilibrium He-to-vacancy ratio of ~2 at 300K contains only 18 He atoms. Accumulation of enough collisions between He atoms inside the bubble and Fe atoms on the interface becomes a real statistical problem. On the contrary, a 5nm bubble occupies 44,399 lattice sites and for a He-to-vacancy ratio of 0.35 at 300K contains 15540 He atoms. See Figs.1a and b for a comparison the smallest and largest studied bubbles at the lowest and highest applied temperatures. The statistical differences make the accuracy of the estimated equilibrium pressure inside He bubbles quite strongly dependent on parameters such as bubble size, He content and temperature.

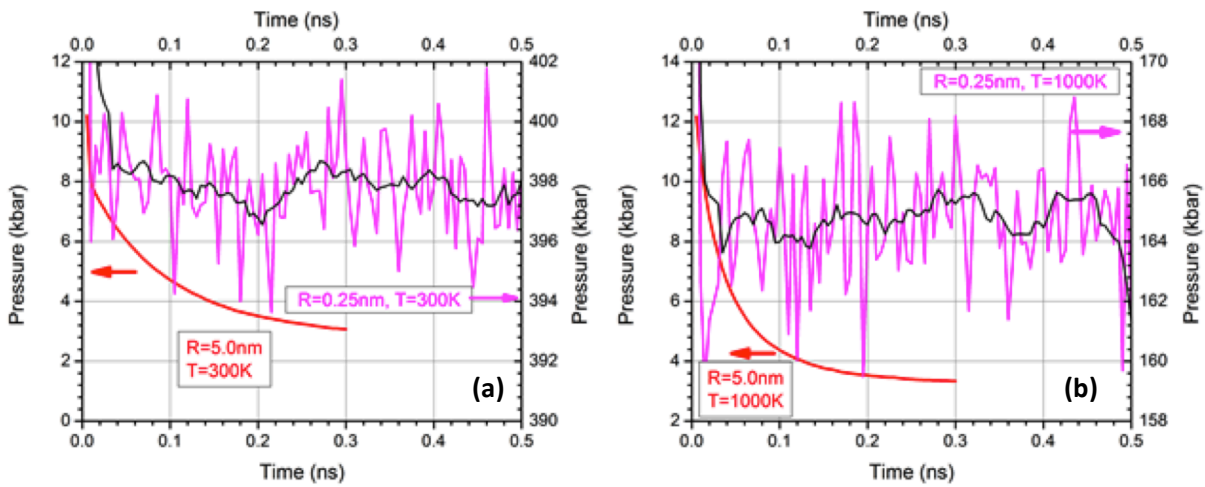

Figure 1. Dependence of the He pressure inside 0.25nm and 5.0nm bubbles during equilibration at a) 300K and b) 1000K. Red and pink lines connect points averaged over 5ps while the black lines average over for 50ps.

We have carried out extensive modeling to identify where the molecular dynamics results are accurate enough. So far we equilibrated large bubbles (>0.5nm) over $6x10^5$ time steps and small ones (<0.5nm) over a million steps at each particular set of conditions. This is equivalent to a physical time equal to 0.3ns and 0.5ns, respectively. Examples of the equilibration process, i.e. the He pressure inside the bubble versus time, are presented in Figs 1a and b for small and large bubbles at the low and high temperature respectively. It can be seen that pressure in the large bubble equilibrates smoothly although 0.3ns appears to be too short a time to obtain complete equilibrium. On the contrary, pressure in the small bubble shows very large fluctuations and does not demonstrate convergence to the equilibrium state. Note that the values shown by the red and pink lines connect points averaged over 5ps while the black lines average over for 50ps.

We have concluded that even the relatively long simulation time of 0.5 ns used so far in our modeling is not sufficient for the smallest bubble studied with a radius of 0.25nm to reach stable

pressures. We are the process of extending the simulation time by about a factor of two for all cases. However, we recognize that it may not be computationally practicable to obtain a highly accurate pressure for the smallest bubbles at the lowest temperatures with a large range of He-to-vacancy ratios. In this case we plan to focus on close-to-equilibrium conditions and, by running the simulations for as long as possible, to obtain the maximum possible accuracy in the equilibrium parameters. Values obtained for other He-to-vacancy ratios will be more approximate but the fitting procedure used to obtain the equation of state will average over the data scatter once the fit to equilibrium conditions is obtained.

FUTURE WORK

The simulation component of this program is nearing the stage where we can treat the results to define He gas equation of state, which is now bubble size dependent. This will be done at the next stage of the program.

REFERENCES

[1] T. Seletskaia, Y. N. Osetsky, R. E. Stoller and G. M. Stocks, "Calculation of Helium Defect Clustering Properties in Iron Using a Multi-Scale Approach," *J. Nucl. Mater.* **351** (2006) 109-118.

[2] D. M. Stewart, Y. N. Osetsky, R. E. Stoller, S. I. Golubov, T. Seletskaia, and P. J. Kamenski, "Atomistic Studies of Helium Defects Properties in BCC Iron: Comparison of He–Fe Potentials," *Philos. Mag*. **90** (2010) 923.

[3] D. M. Stewart, Y. N. Osetskiy, and R. E. Stoller, "Atomistic Study of Helium Bubbles in Fe: Equilibrium State," MRS Proceedings (2011), 1298: mrsf10-1298-q08-04, Materials Research Society 2011, DOI: 10.1557/opl.2011.551, Published online by Cambridge University Press: 15 March 2011.

[4] D. M. Stewart**,** Y. N. Osetskiy, and R. E. Stoller**, "**Atomistic Studies of Formation and Diffusion of Helium Clusters and Bubbles in BCC Iron*, J. Nucl. Mater,* **147** (2011) 1110-1114.