§3. First-principle Calculation of Di-vacancy Formation in Tungsten

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For safety and efficient fuel recycling, less retention of hydrogen isotopes in fusion reactor materials is highly preferable. However, displacements (i.e. vacancy) would be created by plasma ions as well as neutrons, which become additional trapping sites for the hydrogen isotopes. Recently, large defect production has been inferred from measured desorption spectra of deuterium that was implanted into polycrystalline tungsten specimens at room temperature, at implantation energies well below the displacement threshold. Agglomeration of deuterium and vacancies into bubbles were assumed to explain the large desorption fluxes at higher temperatures, although the mechanisms of bubble formation at such low temperatures are still unclear. In the present work, we investigate the influence of ambient hydrogen atoms on the nucleation of vacancy clusters. Di-vacancy formation associated with hydrogen trapping is investigated in terms of nucleation free-energies evaluated using first-principle method.

The Vienna *ab initio* simulation package (VASP ver. 4.6.34) based on density functional theory (DFT) was used for the first principle calculation. In the present calculations, a reference bcc super-cell containing 128 tungsten atoms, a 8×8×8 shifted k-point grid of the Monkhorst-Pack scheme (k-point sampling the Burillouin zone) and a plane wave cut-off energy of 300 eV were used. Numerical convergence was examined by comparing results with different super-cell sizes, k-point grids and plane wave cut-off energies. Ionic configurations and cell shapes were relaxed at constant volumes until forces of every atom in the super-cell became smaller than 0.02 eV/Å. Equilibrium volumes and bulk moduli as well as the total energy were determined by fitting computed energy-volume curves to Birch-Murnaghan's equation of state.

Binding energies of the di-vacancy are evaluated with the first-principle calculations. Present calculations give the largest binding energy for the first-nearest neighbor (1NN) configuration, however earlier calculations using Johnson's model for inter-atomic interaction potentials predicted the second-nearest neighbor (2NN) configuration of the largest binding energy. A favorable configuration of the di-vacancy has been inferred experimentally to be the 1NN by using field ion microscopy (FIM), which is consistent with the present result. It is, however, noted that the present value of binding energy of the 1NN (0.05 eV) is much smaller than a value obtained from the FIM experiment (0.7 eV).

Fig. 1 shows contour plots of the potential energy surfaces of the (a) 1NN and (b) 2NN di-vacancies trapping single hydrogen atom on {200} and {002} planes, respectively. Octahedral sites are known to be favorable trapping sites for the mono-vacancy, and where the

electronic levels for a trapped hydrogen atom and nearest-neighbor tungsten atoms are largely overlapping. In the figure, while the 1NN di-vacancy seems possessing the similar trapping geometry with that of the mono-vacancy, the 2NN di-vacancy shows a remarkable variation of the trapping geometry. The most favorable trapping site is situated at the center of a line connecting the two vacancies, where the trapped hydrogen atom and four nearest-neighbor tungsten atoms may be connected via a covalent bonding with less elastic energy rise. It may be noted that the same location has been reported also as a favorable carbon trapping site in bcc iron. This finding may demonstrate a nontrivial configuration for hydrogen trapping in small vacancy clusters, which is not deduced from straightforward conjectures based solely on a geometrical analogy to surface adsorption. Binding energies of a single hydrogen atom to the 1NN and 2NN di-vacancies are 1.80 and 2.15 eV, respectively, giving almost degenerate formation energies for both V_2H clusters. It is noted that the formation energy of the V_2H clusters coincides with that obtained from the FIM experiment assuming a recommended value of the formation energy of the mono-vacancy, i.e. 3.6 eV.

Using the present first-principle results of the formation energies, nucleation free-energies of the di-vacancy were evaluated. At elevated atomic concentrations of interstitial hydrogen atoms, the evaluated nucleation free-energies indicate that the hydrogen assisted di-vacancy formation becomes more favorable. It is suggested that the formation would be preceded by VH cluster formation.
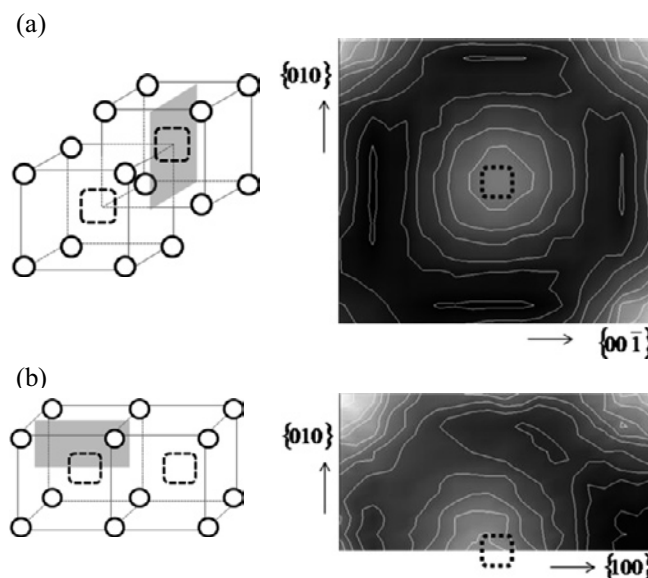
(a)

(b)

Fig. 1　Contour plots of the potential energy surfaces of (a) 1NN and (b) 2NN di-vacancies trapping single hydrogen atom. Dark grey indicates potential valleys, and bright grey potential barriers. Energy interval between two adjacent contour lines is 200 meV. Dotted squares indicate the vacancy positions. (b) plots the contour for only half of the plane because of reflection symmetry with respect to {020} plane.