8.1 PROPERTIES OF VACANCY COMPLEXES WITH H AND He IN TUNGSTEN FROM FIRST PRINCIPLES - G.D. Samolyuk*, Y.N. Osetsky, and R.E. Stoller (Oak Ridge National Laboratory)

OBJECTIVE

Tungsten and its alloys are the primary candidate materials for plasma facing components in fusion reactors. The material is exposed to high-energy neutrons and high fluxes of helium and hydrogen atoms. He and H atoms, being very mobile in the defect-free material bulk, strongly affect the microstructure evolution, mainly through changing the stability of vacancy-type defects. We are studying the properties of single vacancy interactions with hydrogen in W using a first principles approach (density functional method, DFT). We also will calculate interaction of vacancies in complexes of up to six vacancies and their interaction with H/He atoms. The binding energies obtained will be used in mean-field type modeling of deuterium/helium implantation in tungsten with the purpose of comparison with experimental observations.

SUMMARY

It was demonstrated that the formation energy of both single vacancy and six vacancies clusters, the largest cluster investigated in current research, converges for model cells containing 250 atoms. This size is therefore enough to reproduce interaction and formation energy for both H and He atoms. A He atom is strongly attracted to the vacancy with binding energy of 4.6 eV. The di-vacancy clusters are unstable in first nearest (1NN) and second nearest neighbors (2NN) positions and weakly attract each other at 3NN positions. The introduction of H/He stabilizes di-vacancies. The compact 6 vacancies cluster is stable with binding energy of 2 eV

PROGRESS AND STATUS

As an initial effort we analyzed the existing scientific literature on the subject. The analysis demonstrates that there exist contradictions in even such simple value as di-vacancy interactions results. Thus we started our research from the calculation of properties of single vacancy.

All calculations have been done using the plane-wave basis set and PAW pseudo-potential for W with semi core p-states in the valence band, as it realized in VASP package. The Perdew, Burke, and Ernzerhof exchange-correlation function was used. The Brillouin zone summations were carried out over a 4×4×4 BZ grid for modeling cell containing 6x6x6 cubic unit cells (432 atoms) and the grid was increased to keep the same k-pint density in the modeling cell of smaller size. The plane wave energy cut off was 360 eV. The atomic structure was optimized until the forces to all atoms dropped below 0.001 Ry/A.

In the Figure 1 the result for properties of a single vacancy as a function of modeling cell size is presented. The results shown in blue color correspond to case of constant lattice parameter of perfect structure; in the second case, shown in red, the lattice parameter was recalculated to keep constant volume per atoms value.

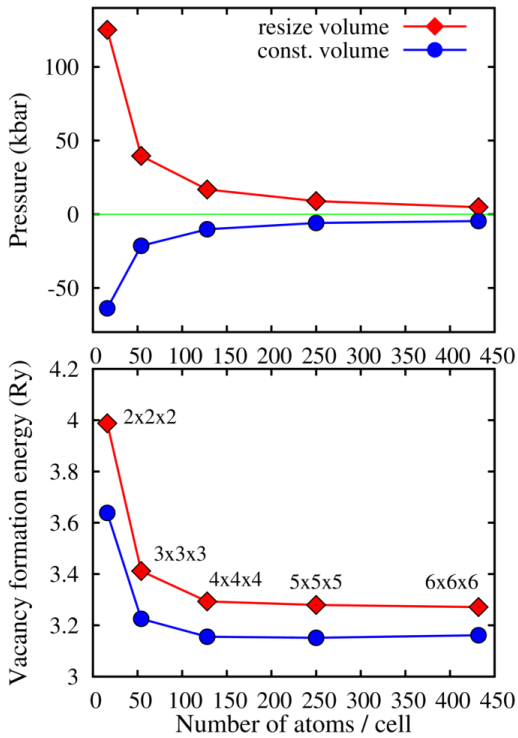

Figure 1. The total pressure and vacancy formation energy as a function of modeling cell size. Two type of calculations results are presented. In the first one shown by red line with diamonds the volume per atom was kept constant. Whereas, by the blue line with circles - the constant modeling cell size results are presented.

As it can be seen, binding energy has converged for 4x4x4 modeling cell containing 128 atoms, however to keep pressure in the system close to zero 5x5x5 modeling cell containing 250 atoms is necessary. The comparison with existing results is presented in Table 1.

Table 1. Single vacancy formation energy, in eV, as a function of modeling cell size together with existing results.

N_{at}	Current	[1]	[2]	[3]
54	3.23	3.23		
128	3.16		3.56	3.17
250	3.15			
432	3.16			

The results obtained are in good agreement with results of existing DFT calculations except formation energy obtained in reference [2], which is in contradiction with all available data.

Interstitial H/He atoms occupy tetrahedral positions in perfect W. The difference between energies of interstitial in tetrahedral and octahedral positions is equal to -0.37 and -0.25 eV for H and He respectively. These energy differences are in agreement with results obtained in Ref. [4].

In the presence of a vacancy, H/He occupy distorted octahedral position shown in Figure 2 as a grey color sphere.

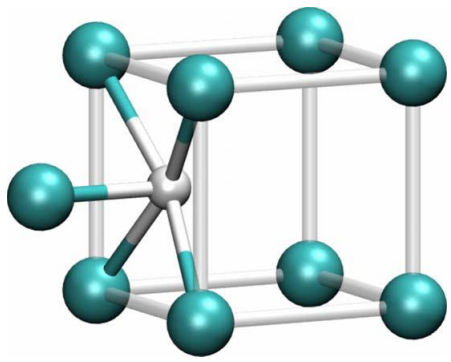

Figure 2. Distorted octahedral position occupied by H/He atom shown by light color sphere in the presence of a vacancy.

While the vacancy formation energy has converged in the super cell of the size 128 atoms (see Figure 1), to preserve total pressure in the system close to zero we need system of the size 452 atoms. The modeling in smaller size model cells has been done for comparison with existing results and to test the convergence. The presence of He atoms, according to our results, increases the total pressure by 1 kbar. It points out that the presence of He in one of the vacancies should lead to binding of H/He with a vacancy and increase the di-vacancy binding energy. The binding energy of one He atom with vacancy is equal to 4.64 eV, which is in agreement with previous results, 4.5 eV obtained in the 4x4x4 modeling cell [4].

In agreement with result obtained for the smaller modeling cell (250 atoms), two vacancies placed in the nearest (1NN) and next-nearest (2NN) neighbors positions repulse each other. The binding energies are equal to -0.11 and -0.46 eV respectively (see Table 2). The interaction between vacancies in third nearest (3NN) neighbor's position is attractive and binding energy is equal to 0.05 eV.

Table 2. Di-vacancy binding energy in eV.

N_{at}	432	128	54 [1]	128 [2]	128 [3]
1NN	-0.11	-0.16	-0.03	0.41	-0.16
2NN	-0.46	-0.48	-0.47	0.19	-0.47
3NN	0.05				0.13

The presence of H atom changes 1NN and 2NN di-vacancy interaction to attraction with binding energy equal to 1.51 and 1.42 eV of 1NN and 1NN respectively.

Table 3. Di-vacancy binding energy in presence of H atom in one of vacancies in eV.

N_{at}	432	128	128 [3]
1NN	1.51	1.30	1.80
2NN	1.42	1.38	2.15

In the presence of a He atom the di-vacancy binding energy changes to 0.13 eV, i.e. interaction is slightly attractive.

Similar to other materials, in tungsten the large size vacancy cluster started to be stable. Thus, binding energy for 6 vacancies, shown in Figure 3, is equal to 2.02 eV in 6x6x6 modeling cell (1.98 in 5x5x5 and 1.89 eV in 4x4x4).

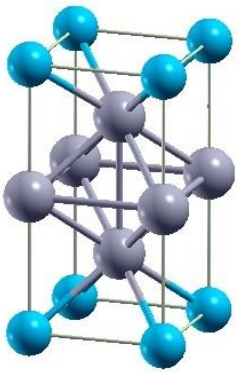

Figure 3. Six vacancies cluster.

Literature

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[4] Becquart C S and Domain C JNM. (2009) 386