8.4 INTERACTION OF INTERSTITIAL CLUSTERS WITH RHENIUM, OSMIUM, AND TANTALUM IN TUNGSTEN—

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OBJECTIVE

The objective of this research is to develop a database of binding energies of interstitial clusters in tungsten to solid transmutation products including Re, Os, and Ta. The database will be used to inform kinetic Monte Carlo simulations of damage accumulation and defect microstructure evolution in bulk tungsten under fusion neutron irradiation.

SUMMARY

In the previous semi annual report [1], we explored the stability of interstitial clusters in W up to size seven. In this report, we study the binding of those clusters to Re, Os, and Ta atoms. For each cluster size, the three most stable configurations are considered to average the binding property. The average binding energy to a Re decreases from 0.79 eV for a size-1 cluster (a [111] dumbbell) to 0.65 eV for a size-7 cluster. For Os, the binding decreases from 1.61 eV for a [111] dumbbell to 1.34 eV for a size-7 cluster. Tantalum is repulsive to interstitial clusters with binding energy ranges from -0.61 eV for a [111] dumbbell to -0.5 eV for a size-7 cluster.

PROGRESS AND STATUS

VASP [2, 3] was used to perform the quantum calculations within the density functional theory (DFT) framework. Core electrons are modeled with accurate projector-augmented-wave pseudopotentials [3]. Electrons in 6s and 5d states are treated as valence electrons. Perdew-Burke-Ernzerhof formulations [4] were employed for the exchange-correlation functionals. Defect formation energies were calculated using cubic 5x5x5 supercells of tungsten's bcc unit cell. The coordinates of atoms and box volume are optimized while maintaining cubic symmetry. In relaxed configurations, the forces are < 0.025 eV/Å and the external pressure < 0.5 kbar. At the end of the relaxations, a static calculation was performed to eliminate errors due to basis incompleteness associated with changes in the simulation cell. A convergence study of the defect formation energies of [111], [110], and [100] dumbbells was performed with respect to the energy cutoff (ENCUT) for the plane waves up to 500 eV. An energy cutoff of 250 eV was found to be sufficient to converge the formation energies to within 20 meV. Therefore, all subsequent calculations were performed with ENCUT = 250 eV.

In our previous study of self-interstitial atom (SIA) clusters, a Monkhorst-Pack [5] k-points grid of 3x3x3 was used. Since then, we perform the convergence study with respect to the k-points grid. We find that a 5x5x5 or denser grid is necessary to converge the formation energy of dumbbells to within 20 meV. Results presented in this report are obtained with the 5x5x5 grid. Table 1 shows the formation energy of [111], [110], and [100] dumbbells, mixed dumbbells, and substitutional solutes. Table 2 shows the binding energy of a size-n SIA cluster corresponding to an $n \rightarrow (n\text{-}1) + 1$ reaction in which the configuration for the (n-1) resultant cluster is taken to be the most stable configuration for a size-(n-1) cluster.

Table 1. Formation energies of Ta-W, W-W, Re-W, and Os-W dumbells in the [111], [110], and [100] orientations, as well as the formation energies of a substitutional Ta, Re, or Os, and a vacancy in W. All energies are in eV. Values in bold are the formation energies corresponding to the most stable orientation of these dumbbells. Note that the Ta-W [100] dumbbell instantaneously relaxes to a W-W [100] dumbbell and a substitutional Ta.

	Ta-W	W-W	Re-W	Os-W
111	**10.04**	**9.90**	9.27	9.02
110	10.46	10.16	**9.21**	**8.68**
100	11.62	11.92	11.20	10.84
Substitutional	-0.46	N/A	0.17	0.74
Vacancy	N/A	3.17	N/A	N/A

Table 2. Binding energy of a size-*n* cluster corresponding to an $n \rightarrow (n\text{-}1) + 1$ reaction. All energies are in eV. The results for the three most stable (1st, 2nd, and 3rd) configurations are presented.

n	1st	2nd	3rd	Average
2	2.49	2.46	1.99	2.31
3	3.64	3.08	2.52	3.08
4	4.69	4.59	3.34	4.21
5	4.74	3.83	3.56	4.04
6	5.41	5.06	4.89	5.12
7	6.74	5.20	5.17	5.70

When an SIA binds to a substitutional solute positioned along its migration path, it forms a mixed dumbbell. Thus, in a mixed dumbbell, the solute atom adopts an interstitial position. Similar to the case of an SIA, when an SIA cluster binds to a substitutional solute located along its migration path, the solute adopts an interstitial site and becomes part of the dumbbell atoms. Therefore, the binding property of SIA clusters with a substitutional solute is studied by replacing one of the conjugate atoms with Re, Os, or Ta. Conjugate atoms are those initially at lattice sites but now sharing the sites with SIAs as dumbbells. Three of the most stable clusters for each cluster size are considered and their binding with a solute atom is explored. From these three clusters, the minimum, maximum, and average binding energies are calculated. The results are presented in Table 3.

Table 3. Binding energy of size-*n* SIA clusters to a substitutional solute obtained by replacing one of the dumbbell atoms with the solute. The minimum, maximum, and average values are in eV and calculated from the three most stable configurations.

n	Re			Os			Ta		
	Min	Max	Ave	Min	Max	Ave	Min	Max	Ave
1	0.79	0.79	0.79	1.61	1.61	1.61	-0.61	-0.61	-0.61
2	0.71	0.82	0.77	1.61	1.69	1.67	-0.72	-0.57	-0.62
3	0.63	0.88	0.76	1.35	1.79	1.57	-0.65	-0.49	-0.59
4	0.66	0.80	0.75	1.40	1.63	1.54	-0.64	-0.51	-0.58
5	0.53	0.77	0.71	1.11	1.59	1.45	-0.62	-0.39	-0.56
6	0.53	0.75	0.68	1.08	1.52	1.41	-0.59	-0.41	-0.53
7	0.41	0.75	0.65	0.81	1.51	1.34	-0.58	-0.35	-0.50

Further simulations to correct for the size effect of the cell are currently in progress. Final results will be presented in Ref [6].

In the meantime, we analyze the interpolation of the binding energy data towards larger clusters. The interpolation is based on the analytical expression of the formation energy $E_f(n)$ of a size-*n* dislocation loop [7, 8]:

$$E_f(n) = a\sqrt{n} + b\sqrt{n}\ln(n) \tag{1}$$

This leads to the binding energy formula:

$$E_b(n) \equiv E_f(1) + E_f(n-1) - E_f(n) \tag{2}$$

$$E_b(n) = E_f(1) - a\left(\sqrt{n} - \sqrt{n-1}\right) - b(\sqrt{n}\ln(n) - \sqrt{n-1}\ln(n-1)) \tag{3}$$

Setting $n = 1$ in Equation (1) yields $a = E_f(1)$, and using $n = 2$ in Equation (3) to solve for b leads to the following equations:

$$b = \frac{(2-\sqrt{2})E_f(1) - E_b(2)}{\sqrt{2}\ln(2)} \tag{4}$$

$$E_b(n) = E_f(1) - E_f(1)\left(\sqrt{n} - \sqrt{n-1}\right) - \left[\frac{(2-\sqrt{2})E_f(1) - E_b(2)}{\sqrt{2}\ln(2)}\right]\left(\sqrt{n}\ln(n) - \sqrt{n-1}\ln(n-1)\right) \tag{5}$$

where the formation energy for a [111] dumbbell is $E_f(1)$ = 9.90 eV and the average binding energy for a size-2 cluster is $E_b(2)$ = 2.31 eV. Figure 1 shows the minimum, maximum, and average binding energy of SIA clusters with respect to an $n \rightarrow (n\text{-}1) + 1$ reaction, as well as the interpolation model of Equation (5). For $n \rightarrow \infty$**,** the binding energy approaches the formation energy of a [111] dumbbell.

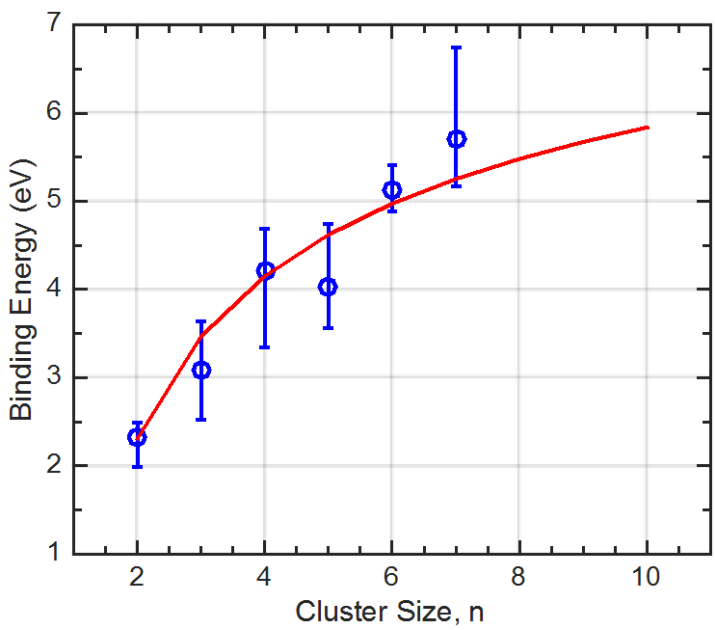

Figure 1. Binding energy of size-*n* SIA clusters with respect to an $n \rightarrow (n\text{-}1) + 1$ reaction. For this work, the average value over the three most stable clusters is plotted with the tic marks above and below the average values representing the maximum and the minimum values. Interpolation curve for large n is based on the formula $E_b(n) = 9.90 - 9.90\left(\sqrt{n} - \sqrt{n-1}\right) - \left[\frac{(2-\sqrt{2})9.90-2.31}{\sqrt{2}\ ln(2)}\right]\left(\sqrt{n}\ln(n) - \sqrt{n-1}\ln(n-1)\right)$**.**

To find the interpolation function for the solute's binding energy to SIA clusters ($E_{bs}(n)$), we assume that the effect of the solute in changing the charge density in the matrix is screened as a function of distance (r) from the solute similar to a screened coulomb interaction, i.e. $\sim\frac{\exp(-\alpha r)}{r}$. This implies that for an infinitely large cluster, the difference between the formation energy of an SIA cluster ($E_f(n)$) and the formation energy of an SIA cluster with a solute atom bound to it ($E_{fs}(n)$) approaches a constant value, say Δ_f. With this assumption, we may write for a loop with a radius r or size n:

$$E_f(r) - E_{fs}(r) = \Delta_f + \frac{c'\exp(-\alpha' r)}{r} \tag{6}$$

$$E_f(n) - E_{fs}(n) = \Delta_f + \frac{c\,\exp(-\alpha\sqrt{n})}{\sqrt{n}} \tag{7}$$

Then the solute's binding energy is given by

$$E_{bs}(n) = E_{sub} + E_f(n) - E_{fs}(n) = E_{sub} + \Delta_f + \frac{c\,\exp(-\alpha\sqrt{n})}{\sqrt{n}} \tag{8}$$

Where E_{sub} is the solute's substitutional formation energy. The values for Δ_f, c, and α are fitted and presented in Table 4. The solute's binding energy and the interpolation curve based on Equation (8) are shown in Figure 2.

Table 4. Fit results of the average binding energy, over the three most stable clusters, of SIAs to a substitutional solute, calculated with Equation (8), where E_{sub} is the formation energy of a substitutional solute, while Δ_f, c, and α are the fitting parameters.

	Re	Os	Ta
E_{sub} (eV)	0.17	0.74	-0.46
Δ_f (eV)	0.448	0.535	-0.021
c	0.195	0.416	-0.155
α	0.0014	0.0012	0.0011
R^2 of the fit	0.69	0.60	0.62

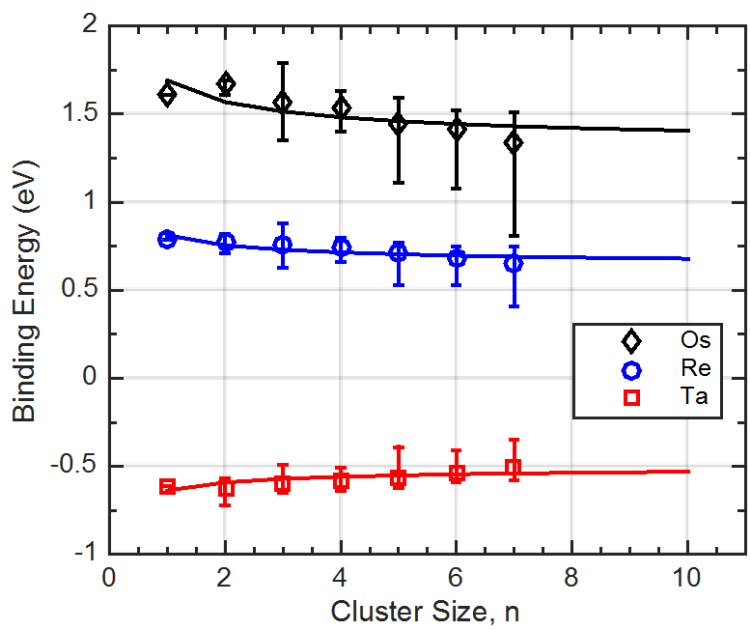

Figure 2. Binding energy of size-*n* SIA clusters to a Re, Os, or Ta atom substitutionally replacing one of the W dumbbell atoms. The data points represent the average over the three most stable clusters. The tic marks represent the maximum and minimum values. Interpolation curves for large n are based on the formula given in Equation (8) with the fitting parameters given in Table 4.

Acknowledgement

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