HELIUM IN IRRADIATED IRON: A MULTI-SCALE STUDY—T. Seletskaia, Yu. N. Osetsky, R. E. Stoller, and G. M. Stocks (Oak Ridge National Laboratory)

OBJECTIVE

A new empirical He-Fe potential was obtained by fitting to results obtained from first principles calculations. Both the formation and relaxation energies of single He defects and small He clusters were accounted for in the fitting process. The new potential consists of a repulsive pair-potential term and a three-body interaction term and was applied in combination with three commonly-used iron interatomic potentials (Finnis-Sinclair, Ackland, Mendelev et al.) and a potential for helium in vacuum by Aziz et al. As an application of the new potential, we evaluated the stability of He-vacancy clusters at zero temperature. The calculated results were similar for all three Fe-Fe potentials. The results obtained with the new potential are consistent with *ab initio* calculations as well as experimental observations of helium desorption reported in the literature.

SUMMARY

Helium is produced in neutron-irradiated metals as the result of (n, α) transmutation reactions and plays a significant role in microstructure evolution and mechanical properties degradation [1,2]. Due to helium's high mobility via an interstitial migration mechanism and its strong binding with vacancies, information on its atomistic behavior is hard to assess from experiments. The only way to obtain such information is from first-principles electronic structure calculations. However, electronic structure calculations can not be used on the time and size scales needed to simulate the important evolution of helium-vacancy clusters that ultimately leads to bubble formation. A multi-scale approach, based on constructing an empirical potential and employing this potential in classical molecular dynamics, seems to be the only practical approach currently available to study He behavior in metals on the desired scale.

The only previous attempt to construct empirical potentials for He in iron resulted in an Fe-He potential obtained by Wilson [3] in the late 1960s. The potential was defined as a pairwise interaction energy for a Fe-He^0 dimer completely ignoring bulk properties of the metal matrix. The latter makes it inappropriate for simulating energy and dynamic properties of He defects in the iron matrix. Electronic structure calculations [4,5] have demonstrated that the Wilson potential predicts the wrong site preference for the He interstitial defect and significantly overestimates the binding energy of one He atom with a vacancy. A pair potential model is not suitable for Fe-He interaction in general because there a pair potential can not accurately describe both the forces and formation energies of He defects [6]. Fe-He interaction originates by electronic hybridization between Fe *d*- and He *s*- electrons. The hybridization is strong enough to change the magnetic moment of He iron neighbors [4] telling us about the complexity of the potential.

In our previous work [7], we presented a Fe-He empirical potential fitted to first-principles results with the high accuracy. The potential consisted of a pair potential part and an embedded energy. The later modifies He-He interaction and makes the potential inapplicable to the problems considering a low density He gas inside the iron void. In this case, He gas is expected to have its vacuum properties. Here we introduce a different model that does not have this deficiency. The form of the potential was inferred from the electronic structure calculations. The potential was used to study He-vacancy cluster stability at zero temperature using the classical molecular statics (MS) technique.

Methodology

In our empirical model of a Fe-He system consisting of I_{Fe} iron atoms and I_{Fe} helium atoms, we have chosen the following functional form for the total energy:

$$E = \sum_{i \in I_{Fe}} \Phi_{Fe}(\rho_i) + \sum_{\substack{i \in I_{Fe} \\ j \neq i, j \in I_{Fe}}} \varphi_{FeFe}(r_{ij}) + \sum_{\substack{i \in I_{He} \\ j \in I_{Fe}}} \varphi_{HeHe}(r_{ij}) + \sum_{\substack{i \in I_{He} \\ j \neq i, j \in I_{He}}} \varphi_{FeHe}(r_{ij}) \qquad (1)$$

$$+ \sum_{\substack{i \in I_{He} \\ j \in I_{Fe} \\ k \neq j, k \in I_{Fe}}} \Upsilon_{He}(r_{ij}, r_{ik}, \Theta_{jik})$$

where the first two terms describe Fe-Fe interaction; the third and the forth terms represent a He-He and a Fe-He pair potentials, respectively; and the fifth term introduces a Fe-He three-body interaction. In our calculations we included three potentials describing the Fe-Fe interaction, *viz.*, those by Finnis and Sinclair [8], Ackland [9], and Ackland et al. [10] based on the work of Mendelev et al. [11]. All Fe-Fe potentials have a many-body term as described by the first term in Eq. 1 which depends on the atomic density ρ_i and a repulsive pair potential, given by the second term as function of the interatomic distance r_{ij}. The discrepancies between *ab initio* calculations and the empirical potentials for pure iron were reduced according to [7]. For He-He interaction term, we use a He-He vacuum pair potential of Aziz et al. (1995) [12].

The empirical Fe-He potential consisting of a pair potential term, $\varphi_{FeHe}(r_{ij})$, and a three-body term, $\Upsilon_{He}(r_{ij}, r_{ik}, \Theta_{jik})$, was obtained by fitting the results of first-principles calculations. The calculations were performed using the Vienna *ab initio* simulation package (VASP) as described in previous publications [4,7]. Our objective was to fit formation and relaxation energies of the single He defect and small He clusters. Interstitial He in both the octahedral and tetrahedral positions and the substitutional He defect (He octa, He tetra, and He sub) [4] were evaluated. He clustering behavior was investigated for both interstitial and vacancy-type defects. These included a He di-interstitial and clusters with two and three He atoms located inside one vacancy (2He, 2He-vac, and 3He-vac) [7].

The long-range part of the pair potential was fitted first using a simple and relatively flexible mathematical form:

$$\varphi_{FeHe}(r_{ij}) = p_1(1 - p_2(\frac{r_{ij}}{p_3} - 1))e^{-p_4(\frac{r_{ij}}{p_3} - 1)} \cdot f_{cut}(r_{ij}), \qquad (2)$$

where $f_{cut}(r_b, r_c, r_{ij})$ is a cutoff function whose first and second derivatives vanish when $r_{ij}=r_b$ and $r_{ij}= r_c$.:

$$f_{cut}(r_{ij}) = (1-x)^3(1+3x+6x^2), \text{ where } x = \frac{r_{ij} - r_b}{r_c - r_b}. \qquad (3)$$

For $r_{ij} < r_b$, $x=0$, and for $r_{ij} > r_c$, $x=1$. $\varphi_{FeHe}(r_{ij})$ has three fitting parameters (p_1, p_2, and p_4) since p_3 is simply a scaling factor.

The parameters were obtained using a least-squares method. Since the three-body interaction is acting only in the interstitial region, the parameters of the pair potential were fitted to the formation energies of He substitutional defect and the formation energies of 2 and 3 He atoms in a vacancy. The smallest Fe-He separation in these configurations is equal to 1.68 Å. Initial guesses for the potential parameters $\{p_i\}$ were used to estimate the sum of squared differences. The minimization of the sum of squared differences was performed by the conjugate-gradient method. However, this procedure does not

guarantee zero forces for the relaxed configurations. Therefore, the obtained potential was used to relax the above configurations by classical MS in a 128-atom supercell as was used in VASP calculations [4,9]. Then the parameters $\{p_i\}$ were varied and relaxation repeated until the minimum sum of squared differences between *ab initio* and MS simulations was reached.

The derived pair potential reproduced He behavior in vacuum but strongly underestimated the formation energies of He interstitials. To fit the energies of the interstitial, we used an exponential function for interatomic distances less then 1.6 Å and a simple polynomial to smoothly join this function with the long-range part of the pair-potential. As a result, the pair-potential is written:

$$\varphi_{FeHe}(r_{ij}) = \begin{cases} \exp(b_1 + b_2 x + b_3 x^2 + b_4 x^3 + b_5 x^4),\ r_{ij} < 1.6\dot{A} \\ a_1 + a_2 x + a_3 x^2 + a_4 x^3 + a_5 x^4 + a_6 x^5,\ 1.6\dot{A} \le r_{ij} < 2.2\dot{A}, \\ \varphi(r_{ij}),\ 2.2\dot{A} \le r_{ij} < 4.4\dot{A} \end{cases} \quad (4)$$

where $\varphi(r_{ij})$ is given by Eq. 2. The parameters of the potential are given in the Table 1.

Table 1. Parameters for pair potential given by Eq. 2 and 5

b_1= -2.142600207811	a_1 = -285.7450302953, eV	p_1=0.167753, eV
b_2= 32.965470333178, Å^{-1}	a_2= 794.5913355517, eVÅ^{-1}	p_2=0.000000
b_3= -52.893449935488, Å^{-2}	a_3= -856.9376372455, eVÅ^{-2}	p_3=2.432258, Å
b_4= 30.970079966695, Å^{-3}	a_4= 452.5323035795, eVÅ^{-3}	p_4=3.727249
b_5= -6.398785336260, Å^{-4}	a_5= -117.6519447529, eVÅ^{-4}	r_b=4.1, Å
	a_6= 12.0878858024 , eVÅ^{-5}	r_c=4.4, Å

The three-body potential term was introduced to improve the fitting for the interstitial properties. It has the following form:

$$Y_{He}(r_{ij}, r_{ik}, \Theta_{jik}) = \sum_{\substack{j \in I_{Fe} \\ k \neq j, k \in I_{Fe}}} f^Y(r_{ij}) f^Y(r_{ik}) \cos^2(\Theta_{jik} - 0.44), \quad (5)$$

where the summation is performed over the Fe neighbors of He atom separated by the distances r_{ij} and r_{ich}, with the functions $f^{ey}(r)$ representing the distance-dependence of the three-body potential and Θ_{jik} is the angle between the radius-vectors r_{ij} and r_{ich} drawn from the He atom as the centre. To guarantee the preference for the tetrahedral site over the octahedral, we subtract an angle of 0.44 red which is equal to the average angle formed by He-Fe vectors in the tetrahedral position minus $\pi/2$. The functions $f^{ey}(r)$ in Eq. 5 are given by Eq. 3, with the right-hand side multiplied by the parameter a^{ye}. The values of a^{ye} and r^j_b were obtained from the fitting process; their values are 0.7 ev$^{e/2}$ and 1.75 Å, respectively. The cutoff of the three-body energy, r^e_{ek}, was chosen to be 2.2 Å.

Results

The results of the fitting procedure for a single He defect and small He clusters are presented in Table 2. It is clear that when the Fe-He potential is used in combination with different Fe-Fe potentials similar results are obtained for the He defects. Since the potential does not have a many-body part that is different in different Fe potentials, it automatically gives the same formation energies of He defects in unrelaxed structures. The relaxation of Fe atoms around a He defect depends on the stiffness of the Fe potential. Since all three empirical potentials used here were fitted to experimental elastic constants, they yield similar atomic relaxation around the He defect.

Table 2. Results of fitting He defect formation energies (eV) in Fe

Defect	VASP*	Fe-Fe potentials		
		Finnis-Sinclair	Ackland	Mendelev
Unrelaxed Structures				
He octa	6.37	6.40	6.40	6.55
He tetra	5.70	5.72	5.72	5.83
He sub	3.99	3.98	3.82	3.74
Relaxed Structures				
He octa	4.60	4.74	4.70	4.57
He tetra	4.36	4.37	4.33	4.26
$He_{i\text{-}mid}$	4.42	4.40	4.37	4.29
He sub	3.73	3.82	3.70	3.75
He-He-vac	6.29	6.49	6.35	6.46
He-He-He-vac	9.09	9.39	9.23	9.37
He-He inter.	8.72	8.59	8.54	8.24

*VASP results for He defects in a vacancy were scaled for the Ackland potential [7].

The formation energies are reproduced to within an accuracy of 0.2 eve. The tetrahedral He interstitial is the most stable in all of the iron matrices. Based on a comparison with the *ab initio* simulation of He migration by Fu and William [13], the new potential accurately describes He interstitial migration [13]. The He migration path from one tetrahedral position to another lies in a <110> direction that does not pass through the octahedral site. The formation energy of a He interstitial at the midpoint of this migration path is denoted by $He_{ir\text{-}mid}$ and is given in Table 2. The new potential somewhat underestimates the formation energy of a He di-interstitial, while overestimating its binding by about 0.2 eve. However, we believe that this inaccuracy for very closely spaced He atoms should have only a weak effect on its future application. Atomic helium clusters are unlikely to be created in significant numbers because He is easily trapped by vacancies. Overall the potential accurately describes the formation energies before and after relaxation which also indicates it's good performance in describing Fe-He forces.

The new Fe-He potential was used to study the properties of He-vacancy clusters at 0 K. The dependence of the binding energy of additional He atoms to a He-vacancy cluster (substitutional He) and the binding energy of an Fe SIA to a He-di-vacancy cluster were investigated as a function of cluster size. The definitions of the binding energies are given in [7]. Periodic boundary conditions were applied to a cubic $10a_0$ x $10a_0$ x $10a_0$ computational cell (a_0 is bcc iron equilibrium lattice parameter). The atomic coordinates were relaxed using a conjugate-gradient method to zero force at constant volume. The results for He atom and Fe SIA binding are presented in Figs. 1(a) and (b), respectively, for simulations performed with the Ackland [9] and Mendelev [10] Fe potentials. The results are qualitatively the same with either iron matrix, with a strong atomic relaxation observed around the He-vacancy complex. The binding energies for small He-vacancy clusters calculated from first principles [7] are also shown in Fig. 1(a). The binding energies calculated with the new potential agree with *ab initio* calculations to within 0.25 eve. The binding energies obtained from Wilson's Fe-He pair potential [13] are also presented for comparison. Wilson's potential systematically overestimates the binding of a He atom to the He-vacancy cluster and underestimates the binding of an Fe SIA.

The binding energy of a He atom to the He-vacancy cluster does not exhibit a simple dependence on the number of He atoms. It initially decreases and then increases, with a local maximum when a total of six He atoms (five He bound to substitutional He) are involved. In this case, a compact He octahedron is formed with a vacant site at the center. For larger numbers of He atoms, the local dilatations produced by the He-vacancy complex are strong enough to begin displacing iron atoms at the periphery of the cluster.

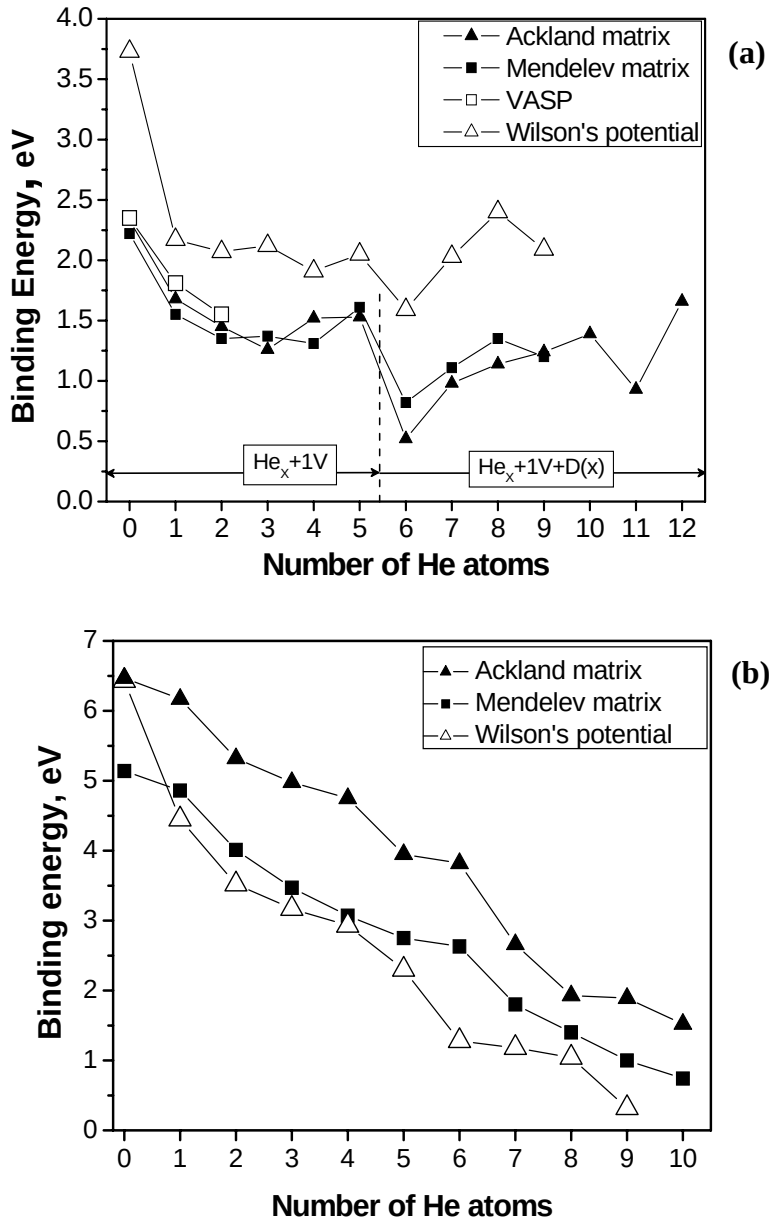

Fig. 1. Binding energy: (a) of He atom to a He-vacancy cluster and (b) an Fe SIA to a He-di-vacancy cluster versus the number of He atoms in the cluster.

This leads to the decrease in binding energy shown when the sixth He atom (a total of seven He) is added to the He-vacancy cluster. The notation D(x) in Fig. 1(a) is meant to indicate that significant matrix distortions occur for the larger He contents. An example of these distortions is shown in Fig. 2 for the case of 11 He atoms bound to the He-vacancy cluster. Eight Fe atoms are displaced by ~0.2 a_{go} in approximately <110> directions to create the extra volume required to accommodate the He. These distributed displacements rather than true Frenkel pair were observed in all the static simulations, and the configuration shown in Fig. 2 suggests the possibility of directly producing Fe interstitial clusters (so-called loop punching) for clusters with greater He content. Dynamic simulations at finite temperature are required to determine if Frenkel pair or interstitial cluster formation is favored.

The strong He binding behavior contrasts with that of an Fe SIA. As shown in Fig. 1(b), the binding energy of an SIA to a He-di-vacancy cluster decreases continuously as the number of He atoms increases. The weaker SIA binding is ultimately a necessary condition for He bubble growth since it

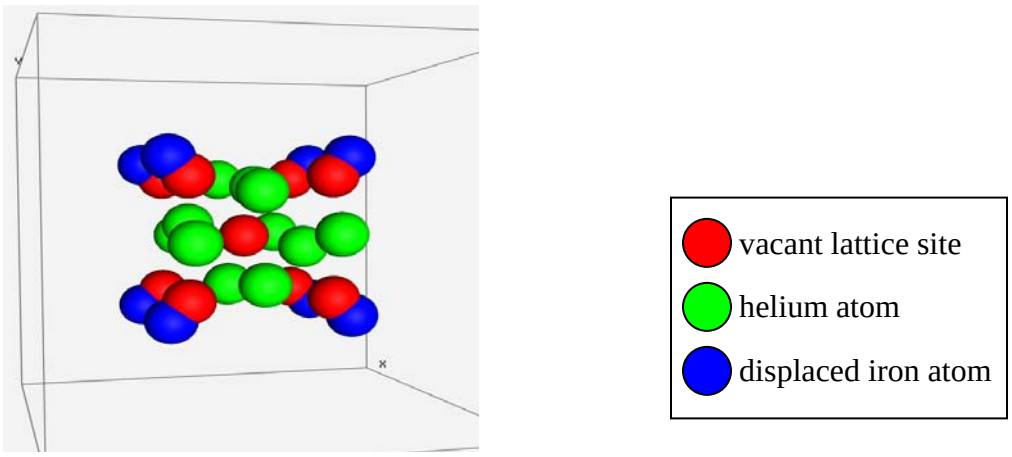

Fig. 2. He-vacancy cluster with a total of 12 He atoms. Initial, true vacancy is shown at center and dilatation-induced defects at the periphery.

favors He-vacancy agglomeration relative to SIA-vacancy recombination for larger He-vacancy clusters.

Conclusions

A multi-scale approach has been applied to study He defect properties in iron. An empirical Fe-He potential, consisting of a pair potential and a three-body term, was fitted to *ab initio* data. When used in combination with different iron potentials, it accurately reproduces the energies of a single He defect and small He clusters. The potential was used to study the zero-temperature properties of helium-vacancy clusters. Depending on the size of the cluster, He atoms are bound with an energy that is generally greater than 1.0 eve, while the binding of a Fe self-interstitial to a He-di-vacancy cluster decreases continuously with increasing cluster size. Although the details of the He-vacancy configurations must be potential dependent to some degree in these static simulations, the physical mechanisms are believed to be accurately predicted. The Fe-He potential that has been developed represents a substantial improvement over currently-available pair potentials, is relatively simple, and can be efficiently applied in large-scale molecular dynamics simulations.

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