The Formation Energies and Binding Energies of Helium Vacancy Cluster: Comparative Study in Ni and Pd

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Abstract. Molecular dynamics calculations are performed to calculate the formation energy for helium in Ni-vacancy and Pd-vacancy clusters. The binding energies of helium and metal self-interstitial atoms (SIA) to the helium-vacancy cluster are also determined. The comparison of these energies indicates that helium to vacancy ratio (He/V) for helium in Pd is much higher.

1. Introduction
When inert gases are introduced into solids, it tends to cluster and precipitate into bubbles. Studies of helium at point defects and helium self-trapping have advanced our understanding of helium in metals\textsuperscript{[1,2]}. Helium atoms energetically prefer to occupy the position, which have lower electronic density in metals. Because of filled electronic shell for Pd, the solubility of helium atoms in Pd may be larger than in Ni. In the present study, molecular dynamics (MD) is performed to calculate the formation energies of helium-vacancy clusters in Ni and Pd. The comparison of the binding energies of a vacancy, a helium atom and a metal atom to helium-vacancy cluster in Ni and Pd, will provide an atomistic understanding for solubility of helium in Ni and Pd.

2. Simulation approach
The accuracy of the potentials used to determine the interaction between atoms is essential to the success of calculation. For the atomic interaction three potentials are employed in the present calculation. To describe the interaction between metal atoms, a potential\textsuperscript{[3]} based on the Embedded Atom Method (\textit{EAM}) is used, the potential has been proved that can describe the defect properties of transition metals\textsuperscript{[4]}. He-He potential employs the Lenard-Jones potential\textsuperscript{[5]} which has been widely used to study the behavior of helium in metals\textsuperscript{[6]}. He-metal potentials are obtained by fitting the free-electron helium-metal pair potentials\textsuperscript{[7]}. The solubility of helium in metals is described by the binding energies of a helium atom ($E_b(He)$) and a self-interstitial metal atom ($E_b(M)$) to helium-vacancy cluster, which are calculated from the following equations:

$$E_b(He)=E(He,V)+E(He)-E(He,V)$$
$$E_b(M)=E(He,V_m)+E(SIA)-E(He,V_m)$$

$E(He,V)$ is the formation energy of helium-vacancy cluster with n helium atoms in a void of m vacancies, $E(V)$ is single vacancy formation energy of metal, $E(He)$, is the formation energy of helium in an interstitial site and $E(SIA)$ is the self-interstitial formation energy of metal. The defect formation energy is determined by comparing the energies of a crystal containing defects with a crystal of the same number of atoms on their perfect lattice sites. Three-dimensional periodic cell of $10a\times10a\times10a$ is used, where $a$ is the lattice constant. The structure of the pure void is determined by beginning with a
single vacancy, and repeatedly removing the atom, which has the largest potential energy, thereby creating another vacancy. In order to fully relax the atoms, anneal molecular dynamics is adopted. The positions of the atoms are relaxed to their minimum energy configuration, and then the formation energies of helium-vacancy cluster are calculated.

The present calculated result indicates that five atoms cluster together in a perfect Ni and Pd lattice is sufficient to spontaneously displace a lattice atom, thereby creating a Frenkel pair and a deeply-bound helium cluster. The result consists with previous study\textsuperscript{[8]} Fig.1 shows the calculated binding energy of helium to a helium mono-vacancy cluster for Ni compares with earlier Wilson’s calculation\textsuperscript{[8]}. The agreement between the two calculated values shows that the present calculated method is reasonable.

![Figure 1](image1.png) ![Figure 2](image2.png)

**Figure 1.** Comparison of the binding energies of the last helium to helium mono-vacancy cluster between the present and Wilson’s calculations.

**Figure 2.** Formation energy of Helium-to-vacancy cluster with 12 vacancies for Ni and Pd versus number of helium atoms.

### 3. Result and discussion

#### 3.1 Formation energy of helium-vacancy cluster

The formation energy of helium-vacancy cluster is the foundation of calculating the defect binding energy. Fig.2 shows the formation energies of helium-to-vacancy cluster with 12 vacancies are in dependence on number of helium atoms. It can be seen that for helium in Ni, the formation energy of helium-vacancy cluster is increasing with the increasing of helium atoms. However, for helium in Pd, the formation energy of helium-vacancy cluster almost keeps a constant with the introducing of helium until the helium to vacancy ratio is greater than 1. It can be explained that with similar closed-shell electronic configuration for helium and Pd, additional helium atoms seems to refill the vacancies in Pd and reducing the formation energy of vacancies.

#### 3.2 Binding energy of helium to helium-vacancy cluster

Considering the stable configuration of the helium atoms in a helium-vacancy cluster (He\textsubscript{V\textsubscript{n}}) primarily depends on the ratio of Helium-to-vacancy (He/V) of the cluster instead of the number of helium atoms\textsuperscript{[8]}. Fig.3 and Fig.4 show the binding energy of a helium atom to a helium-vacancy cluster as a function of the Helium-to-vacancy ratio. The helium binding energy represents the energy required to bind the n-th helium atom in a helium-vacancy cluster. Notes that for the small ratio of He/V the binding energies approximately equal to the formation energy of interstitial helium (the energy is 4.06eV and 2.38eV for in Ni and Pd, respectively). It shows that helium is most strongly bound to large voids containing little helium, because the helium exists in a nearly free state. The high binding energies also explain the formation of helium bubbles. In addition, there are different characters for helium in these two metals. In both metals, with the increasing the He/V ratio, the
helium binding energies gradually decrease, and for helium in Ni, the binding energy increases when the ratio of He/V is greater than 5. Such an increase for helium in Pd cannot be observed up to the ratio of 7. The increase of helium binding energy for helium in Ni when He/V ratio is greater than 5 can be contributed by the collective motion of helium atoms in the cluster which produces bubble pressure large enough to push a metal lattice atom off its normal site and spontaneously creates additional vacancy. The additional vacancy results in a decrease He/V, the calculated result is consist of the previous theoretic results[11]. As shown in Fig 4, the binding energy of helium to a helium-vacancy cluster in Pd decreases to near a constant value about 1.5eV. It can be concluded from the helium binding energy that the density of helium in Pd vacancy without production of additional vacancies is greater than in Ni vacancy, namely the capability of holding helium of palladium is stronger.

3.3 Binding energy of metal atoms to helium-vacancy cluster

Figure 3. Binding energy of a helium atom to helium-vacancy cluster in Ni versus helium to vacancies ratio.

Figure 4. Binding energy of a helium atom to helium-vacancy cluster in Pd versus helium to vacancies ratio.

Figure 5. Binding energy of a metal atom to helium-vacancy cluster in Ni versus helium to vacancies ratio.

Figure 6. Binding energy of a metal atom to helium-vacancy cluster in Pd versus helium to vacancies ratio.
Fig. 5 and Fig. 6 show the binding energy of Ni and Pd atoms to a helium-vacancy cluster as a function of helium to vacancy ratio. It is similar for helium in these two metals that the metal binding energies nearly equal to the Frankel pair formation energy when the helium to vacancy ratio is low, and gradually decrease with the increasing of the He/V ratio. It can be explained that the collecting of helium atoms enables the metal atoms surrounding the cluster to be emitted from the cluster as an SIA (i.e. loop punching). However, when the ratio of He/V is greater than approximately 5, the binding energy of Ni atom to a helium-vacancy cluster dramatically increases. Considering the metal binding energy depends on the ratio of He/V, the increasing of binding energy can be contributed by the effective decrease of helium-to-vacancy ratio. Morishita\(^{9}\) has illuminated that the competitive processes take place between helium emission and SIA emission from a helium-vacancy cluster, both of which result in a decrease of helium to vacancy ratio. Fig 4 and Fig 6 show that for helium in Pd, the helium binding energy is always less than metal binding energy until the helium to vacancy ratio equal to 7, so the competitive processes is not expected to take place. However, for helium in Ni, when the helium to vacancy ratio nearly equals to 5, the metal binding energy is less than the helium binding energy and the competitive processes start to take place.

4. Conclusions

Using a molecular dynamics technique, the formation energy of helium-vacancy cluster, the helium and metal atoms binding energies to helium vacancy cluster in Ni and Pd are calculated. By comparing these energies, it can be concluded that the maximum He/V ratio without spontaneous creation of vacancies can reach 7 for helium in Pd vacancies and only reach 5 for helium in Ni.

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Reference

[1] J.B.Adams and W.G.Wolfer, 1989 J.Nucl. Mater. 166, 235.
[2] W.D.Wilson, M.I.Baskes and C.L.Bisson, 1976 Phys Rev B. 13, 2470.
[3] W. Hu, 2004, International Conference on New Frontiers of Process Science and Engineering in Advanced Materials, Nov, 24-26, Kyoto, Japan. To be published in “Materials Science Forum”.
[4] J. Yang, W. Hu, H. Deng and D. Zhao, 2004 Surf. Sci. 572, 439.
[5] Allen.M.P. and Tildesley.D.J, 1987, Computer Simulation of Liquids (New York: Oxford University press) P21.
[6] L. Wang, X. Ning, 2003 Chin. Phys. Lett. 20, 1416.
[7] M.I.Baskes and C.F.Melius, 1979 Phys.Rev.B. 20, 3197.
[8] W.D.Wilson, 1983 Rad.Eff. 78, 11.
[9] K.Morishita, R.Sugano, B.D.Wirth, T.Diaz de Rubia, 2003 Nucl Instrum and Meth B. 202,76.
[10] S.Sharafat, N.M.Ghonicm, 1984 J.Nucl.Mater. 122, 532.
[11] W.G.Wolfer, 1988 Philo.Mag A. 58, 285.