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Vacancy trapping mechanism for hydrogen bubble formation in metal

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We reveal the microscopic vacancy trapping mechanism for H bubble formation in W based on first-principles calculations of the energetics of H-vacancy interaction and the kinetics of H segregation. Vacancy provides an isosurface of optimal charge density that induces collective H binding on its internal surface, a prerequisite for the formation of H_2 molecule and nucleation of H bubble inside the vacancy. The critical H density on the vacancy surface before the H_2 formation is found to be $10^{19}-10^{20}$ H atoms per m^2. We believe that such mechanism is generally applicable for H bubble formation in metals and metal alloys.

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The interaction between hydrogen (H) and metal is one of the most important topics in materials physics, having a broad range of technological implications. The bonding of H with metals determines the capacity of H storage in and desorption rate of H_2 from the metal hydrides.[1,2] For metal catalyst to assist the production of H_2 via a chemical reaction, the H-metal interaction plays an important role.[3] The H-metal interaction is also responsible for the H embrittlement in metals.[4] Furthermore, in a fusion reactor, metals are used as the plasma facing material (PFM) that is exposed to extremely high fluxes of H-isotope (deuterium-tritium) ions.[5] Consequently, understanding the interaction between H and a metal PFM has a direct impact on the design and operation of a fusion reactor.[6]

Despite many years of research, many fundamental aspects underlying the H-metal interaction remains poorly understood because of the very complex nature of this interaction. One mysterious phenomenon is H bubble formation in metals. H bubble formation and blistering is a common cause for degrading mechanical properties of metals.[5] H has been shown to assist vacancy formation in various metals such as W, Ni, Cr, Pd and Al.[5,7–9] On the other hand, H-isotope ions are seen to be trapped by the vacancy in earlier theoretical predictions and experimental measurements in different metals including Pd, Ni, Mo, Nb, Fe, and Cu,[10–13] which suggested that the trapping energy is still favorable up to six deuterium (D) atoms. However, the microscopic atomic-level relationship between H bubble formation and vacancy is not be revealed.

In this Brief Report, we investigate the interaction structure, energy, and kinetics between H and vacancy in W using first-principles calculations. We demonstrate that vacancies serve as trapping centers to cause H to segregate onto their internal surface by providing an optimal H-embedding isosurface of charge density. Formation of H_2 molecule and hence nucleation of H bubble will be triggered after the number of H reaches a critical density. Our choice of choosing W as a model system is partly because W and W alloys are considered as the most promising PFMs due to their low sputtering erosion and good thermal properties, and it is experimentally demonstrated that high fluxes of H induces the surface roughening and blistering in W.[14,15] We believe the general conclusions we draw from W are applicable to other metals.

Our first-principles calculations were performed using the pseudopotential plane-wave method implemented in the VASP code[16] based on the density-functional theory. We used the generalized gradient approximation of Perdew and Wang[17] and projected augmented wave potentials[18] with a plane-wave energy cutoff of 350 eV. The bcc W supercell of 54 atoms containing a monovacancy and of 128 atoms containing a monovacancy or a divacancy have been used, and their Brillouin zones were sampled with $(5\times5\times5)$ and $(3\times3\times3)$ $\boldsymbol{k}$ points by the Monkhorst-Pack scheme,[19] respectively. Both supercell size and atomic positions were relaxed to equilibrium, and energy minimization was converged until the forces on all the atoms are less than 10^{-3} eV Å^{-1}.

First, we examined the H behavior in the intrinsic bulk W.[20] We found a single H is energetically favorable sitting at the tetrahedral interstitial site (TIS) (Refs. 20 and 21) with an embedding energy of −0.24 eV in reference to the H-chemical potential $\mu_H=-2.26$ eV.[22] We also found that two H atoms tend to pair up at two neighboring TIS, similar to the cases in other metals,[23] along the $\langle 110\rangle$ directions with a binding energy of 0.02 eV. However, the equilibrium distance of the H-H pair is ~2.22 Å, much longer than the H_2 bond length of ~0.75 Å. It implies that H atoms cannot bind together to form a H_2 molecule in the intrinsic bulk W.

Physically, the H-embedding energy in a metal can be understood approximately in terms of the H-embedding energy in a homogeneous electron gas.[24,25] The H-embedding energy decreases monotonically with decreasing electron density until reaching the minimum at the optimal density of $n_0 \approx 0.018$ $e/\text{Å}^3$.[24,25] Since the electron density everywhere in bulk W (as well as in most metals) is much higher than n_0, the H generally has the lowest embedding energy at where the electron density is the lowest. In W, the H-embedding

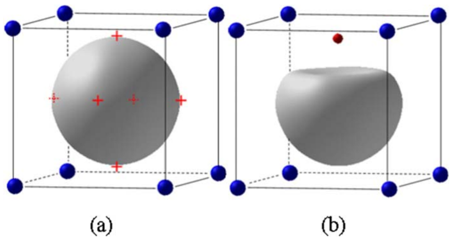

(a) (b)

FIG. 1. (Color online) Isosurface of optimal charge for H binding at a vacancy. The larger blue balls and the smaller red ball represent W and H atoms, respectively. (a) Without H. The crosses mark the 6 minimum-energy H binding sites on the isosurface. (b) With one H.

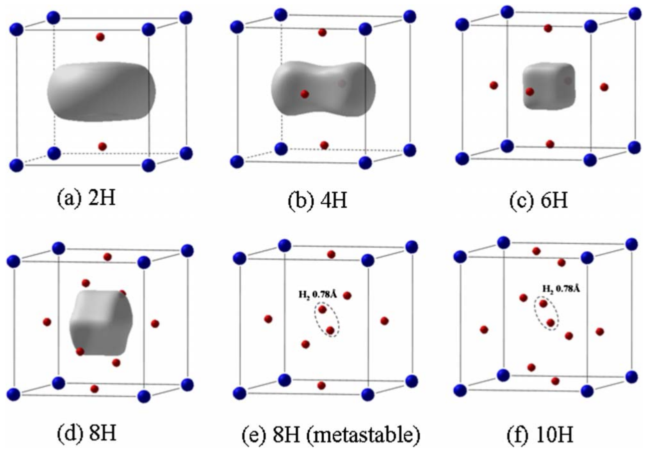
energy is found to be lower at the TIS than the octahedral interstitial ste (OIS) by ~0.38 eV, with the density ~0.27 $e/\text{Å}^3$.

Apparently, in order to further lower the H-embedding energy, it is desirable to create a structure that will further decrease the electron density. Naturally, vacancy can lower the electron density in its vicinity providing an effective mechanism to meet this requirement. We thus calculate the H-embedding energy in the vicinity of a vacancy. The energy minimization finds the most stable site for H to be at an off-vacancy-center position (~1.28 Å from the vacancy center) close to an OIS (Fig. 1), similar to behavior of H isotope ion in other metals.[10] The H binding energy at this site is −1.18 eV lower than that at the TIS in bulk W consistent with the previous studies[26,27]

The main reason for H having a much lower embedding energy at the vacancy site is that there exists a low electron-density region in the vicinity of the vacancy. We found that H prefers to bind onto an isosurface of the same charge density (0.11 $e/\text{Å}^3$) surrounding the vacancy, and its binding energy is about the same on the isosurface with six minimum sites very close to the six OIS's next to the vacancy, as indicated in Fig. 1(a). The binding energy at the other sites on the isosurface is ~0.20 eV higher than the minimum sites, reflecting the additional effect of atomic structure.

The above results indicate that H and vacancy are strongly attractive in metals consistent with previous studies.[5,10–13,28] The extra binding energy of H with vacancy means the vacancy formation energy will be lowered by the presence of H in comparison with that in the intrinsic metal, which explains the experimental observation of H assisted vacancy formation in various metals.[5,7,8] Furthermore, the strong binding between H and vacancy implies that the vacancies can act as trapping centers which drive the H to segregate toward the vacancies providing the necessary prerequisite step for H bubble formation. To investigate this possibility, we have calculated the binding energies of additional H atoms segregating to the vacancy and determine how many H atoms a vacancy may accommodate.

We bring the H atom one by one to the vacancy and minimize the energy to find the optimal-embedding site at each step, as illustrated in Fig. 2. The first six H atoms occupy one by one the six "close-to-OIS's" surrounding the vacancy on the isosurface of optimal charge density, as seen from Fig. 1(b) to Figs. 2(a)–2(c). The additional H atoms tend to occupy randomly on the isosurface [Fig. 2(d)]. It is important to note that as more H atoms are added, the surface of optimal density shrinks so that there will be less available optimal-density sites to accommodate additional H. Eventually, when H atoms exceed a critical density, there exists no longer isosurface for H binding and instead a H_2 molecule forms at the center of vacancy [see Figs. 2(e) and 2(f)].



(a) 2H (b) 4H (c) 6H
(d) 8H (e) 8H (metastable) (f) 10H

FIG. 2. (Color online) Atomic configuration and the isosurface of optimal charge for H for different number of embedded H atoms at the monovacancy. The atom labels are the same as in Fig. 1.

In Fig. 3, we plot the average H-embedding energy (or trapping energy) per H as a function of the number of H inside the vacancy. We may understand the binding of H and vacancy as the following. Each H gains a binding energy of $E_0 = -1.18$ eV as it sits on the isosurface. As more H atoms are added, they experience a repulsive interaction with each other. Assuming the H-H repulsion is additive and the repulsion energy scale as $\sim\exp(\alpha r^{-2})$, where $r = n^{-1/2}$ is the H-H separation and n is the density of H on the isosurface.[29] Then, the H-embedding energy per atom can be derived as

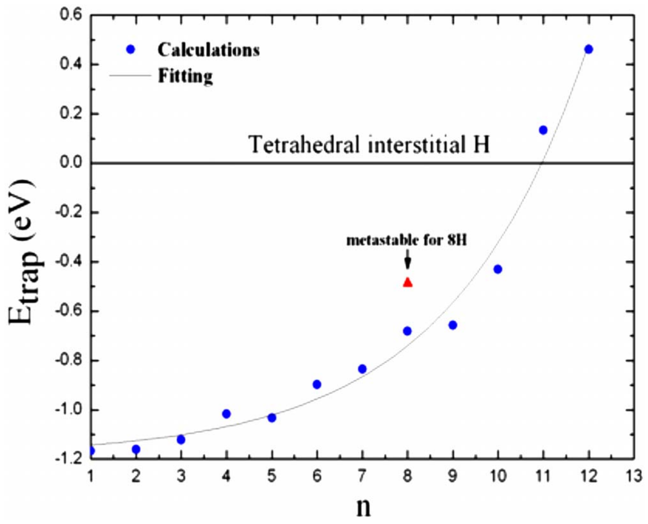


FIG. 3. (Color online) The average H-embedding energy per H as a function of the number of H embedded at the monovacancy in W. The zero-point energy is the energy of H in the TIS far away from the vacancy.

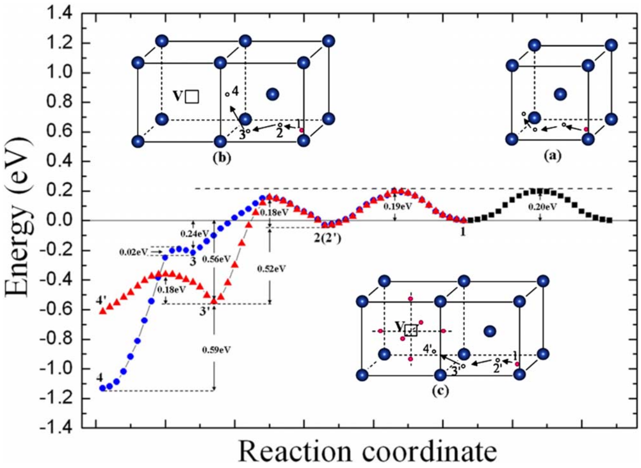


FIG. 4. (Color online) H diffusion energy profile and diffusion paths (arrows) in W. (a) H diffusion from one TIS to another in intrinsic W. (b) H diffusion toward an empty vacancy. Sites 1, 2, and 3 are the 3NN, 2NN, and 1NN TIS of the vacancy, respectively. Site 4 is one of the 6 most stable sites at the vacancy. (c) H diffusion toward a vacancy occupied with 6 H. Site 1, 2, and 3′ are the 3NN, 2NN, and 1NN of the vacancy, respectively. Site 4′ is the most stable site for the 7th H. The atom labels are the same as in Fig. 1.

$$E_{\text{trap}} = E_0 + \beta \exp(\alpha n), \qquad (1)$$

which gives an excellent fit to the calculation results with $\alpha = 19.86$ Å^2 and $\beta = 0.033$ eV, as shown in Fig. 3.

The average H-embedding energy inside a vacancy is lower than that at the TIS far away from the vacancy (set as the zero-point energy in Fig. 3) up to 10 H, beyond which the H-embedding energy becomes positive. Thus, it is energetically favorable for a monovacancy to trap as many as 10 H until a H_2 molecule is formed inside the vacancy. The embedding energy becomes higher with increasing H occupancy up to six H atoms, which agrees well with the earlier study for other metals.[13] Additionally, there is a metastable configuration with 8H in which a H_2 molecule is formed at the center of the vacancy with the other 6 H remaining on the isosurface [Fig. 2(e)], whose energy is ~0.2 eV higher than the stable configuration with all 8 H on the isosurface [Fig. 2(d)]. The H-H distance of the H_2 formed at the center of vacancy (0.78 Å) is very close to that of free H_2 (0.75 Å).

Clearly, the above results demonstrate the thermodynamic feasibility of H segregation toward a vacancy trap so as to initiate H bubble formation. Next, we investigate the kinetic process for such trapping mechanism. We calculated the energy barriers for H atoms diffusing one by one from a far away bulk TIS to the vacancy using a drag method.[30]

Away from the vacancy, H atoms jump from one TIS to another with a diffusion barrier of 0.20 eV, as shown in Fig. 4(a). As they move close toward a vacancy, their diffusion barrier is reduced to 0.19 eV and 0.18 eV at the 3NN and 2NN TIS of the vacancy, respectively, i.e., the site 1 and 2 (2′) in Fig. 4(b) [Fig. 4(c)]. The first 6 H jumps into the vacancy from the 1NN TIS [site 3 in Fig. 4(b)] into vacancy occupying one of six minimum sites [Fig. 1(a)], with a much reduced barrier of 0.02 eV. The seventh and subsequent H jumps into the vacancy from the 1NN TIS [site 3′ in Fig. 4(c)] into vacancy occupying a random site on the isosurface, with a larger barrier of 0.18 eV. Also, the H binding energy at the TIS next to the vacancy becomes lower. The binding energy of the first 6 H at site 3 is 0.24 eV than at site 1, and that of the last 4 H at site 3′ is 0.56 eV than at site 1, as shown in Fig. 4. This indicates a downhill "drift" diffusion of H toward vacancy.

Thus, we have now revealed a "vacancy trapping mechanism" for H bubble formation in W. By providing an isosurface of optimal charge density for H binding, the vacancy causes a "directed" H diffusion (segregation) toward it and traps H atoms up to a critical density before H_2 formation. For a monovacancy in W, the critical density is found to be 0.13 H atoms per Å^2, i.e., $10^{19}-10^{20}$ H atoms per m^2. With this critical density, one expects that vacancy clusters and voids can trap more H atoms to form H bubbles containing multiple H_2 molecules. For example, we estimated a divacancy in the [111] direction with a surface area of ~100 Å^2 may trap ~15 H atom and two H_2 molecules, which is indeed confirmed by our calculations.

Furthermore, vacancy concentration and temperature can have large effect on the formation of H_2. H may distribute uniformly at the vacancies instead of gathering into a monovacancy to form a H_2 molecule for the low H concentration case. If the H concentration is very high, e.g., in an environment of H plasma in nuclear fusion Tokamak, the supersaturated H can result in the formation of H_2. Recent experiments show that W has been irradiated by high fluence ($10^{22} \sim 10^{27}/\text{m}^2$) D plasma,[14] leading to the formation of H_2 bubbles. On the other hand, the vacancy concentration increases with the increasing temperature. Consequently, there should exist a critical concentration for the formation of the H_2 molecule corresponding to a critical temperature. As long as the temperature is lower than certain critical value, the vacancy trapping mechanism for H_2 bubble formation we proposed should be applicable. Experimentally it is shown that H_2 bubble can be formed at a temperature lower than ~700 K.[14]

Although our calculations are one for the W single crystal, the vacancy trapping mechanism can be generalized to polycrystalline W as well as other metals and metal alloys. This is because all the vacancylike defects such as vacancy clusters, void, and grain boundary with more space can provide the optimal charge surface to facilitate collective H binding on their internal surfaces, giving rise to the formation of H_2 molecules and nucleation of H bubbles.

In conclusion, we propose a generic vacancy trapping mechanism for H bubble formation in metals based on systematic first-principles calculations. Vacancy reduces charge density in its vicinity to provide an isosurface for collective H binding, causing H segregation and hence H bubble nucleation when H density reaches a critical density on the internal vacancy surface. We provide the quantitative microscopic parameters related to the atomic-level thermo-kinetic trapping processes. We believe similar mechanism can apply to vacancylike defects such as vacancy clusters, void, and grain boundaries which can all open up a space with reduced change density surface to increase H binding, and hence functions in both crystal and polycrystalline metal and metal alloys.

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