



Communication

Fundamental effects of hydrogen on cohesion properties of Cu/W interfaces



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ARTICLE INFO

Keywords:

- A. Cu/W interface
- C. Hydrogen doping
- D. Interface cohesion

ABSTRACT

First principles calculation is used to investigate the thermodynamic stability of hydrogen at Cu/W interfaces and the effects of hydrogen on cohesion properties of Cu/W interfaces. It is revealed that the solution energies of H atom at the W lattice are more positive than those of H at the Cu/W interface and Cu lattice, suggesting that H atoms in the W lattice should have a tendency to diffuse into the Cu/W interface and Cu lattice. Calculation also shows that the location of interstitial H atom has an important influence on interface cohesion properties, e.g., H atom located just at the very interface area between W and Cu interface layers could dramatically decrease the interface strength of the Cu/W interface, which seems hostile to the performance and lifetime of the Cu/W interface. The derived results are in good agreement with experimental observations in the literature, and are discussed in terms of electronic structures, which could provide a deep understanding to the effects of interstitial H on various cohesion properties of Cu/W interfaces.

1. Introduction

The W-Cu system has raised great research interests during the past decades, and has been widely used as nuclear fusion components, heat sinks in microelectronics, welding electrodes, high voltage electrical contacts, and packing materials, etc. [1,2]. Specifically, tungsten (W) is well considered to be promising plasma facing materials in fusion reactors due to its high melting point, excellent high-temperature mechanical properties, good sputtering resistance, and low deuterium/tritium retention, etc. [3–5], while copper (Cu) and its alloys have been commonly regarded as heat sinks of W materials owing to their wonderful thermal conductivity, good radiation resistance, and favorable mechanical strength, etc. [6–8]. It is well known that the cohesion properties of W-Cu interfaces play important roles in the lifetime and performance of various W-Cu products [9–12]. Very recently, the interface strength and interface energy of various W-Cu interfaces have been derived by means of first principles calculations [13].

Hydrogen (H) and its isotopes should be abundant in W materials during the process of fusion reactions, and would also possibly enter the Cu lattice [8,10,14–16]. Regarding H behaviors in W or Cu lattices, experimental studies in the literature have been mainly focused on H ion irradiation [8,10], H trapping [15–18], and H retention [14], etc. In addition, theoretical methods have been also conducted to find out H blistering, H solution, H diffusion, and H adsorption in W or Cu [17,19–26]. It should be pointed out that H would probably also reach the Cu/W interface regions, and influence the cohesion between W and Cu atoms. As to the effects of H on various properties of Cu/W

interfaces, however, there is no any research report so far in the literature.

By means of highly accurate first principles calculation based on density functional theory [27], the present study is dedicated to find out the location and stability of hydrogen at Cu/W interfaces, and to systematically reveal the effects of hydrogen on interface strength of Cu/W interfaces. Moreover, H behaviors in W and Cu bulks are also derived for the sake of comparison. It will be shown that H location would have an important effect on interface properties, and the calculated results could provide a deep understanding of cohesion properties of Cu/W interfaces with the doping of H atom.

2. Computational methods

The first-principles calculation is based on the well-established Vienna *ab initio* simulation package (VASP) within the density functional theory (DFT) [28]. The calculation is performed in a plane wave basis, using the projector-augmented wave (PAW) method [29]. The exchange and correlation items are treated by the generalized gradient approximation (GGA) of Perdew et. al [30], and the cutoff energies are 400 eV for plane wave basis. For the Brillouin zone sampling, the temperature smearing method of Methfessel–Paxton [31] is used for relaxation calculation and the modified tetrahedron method of Blöchl–Jepsen–Andersen [32] is performed for static calculation.

The interface structure between the close-packed surfaces of FCC Cu (overlayer) and BCC W (substrate), i.e., (111)Cu/(110)W, is selected as a typical example to find out the effects of H on cohesion

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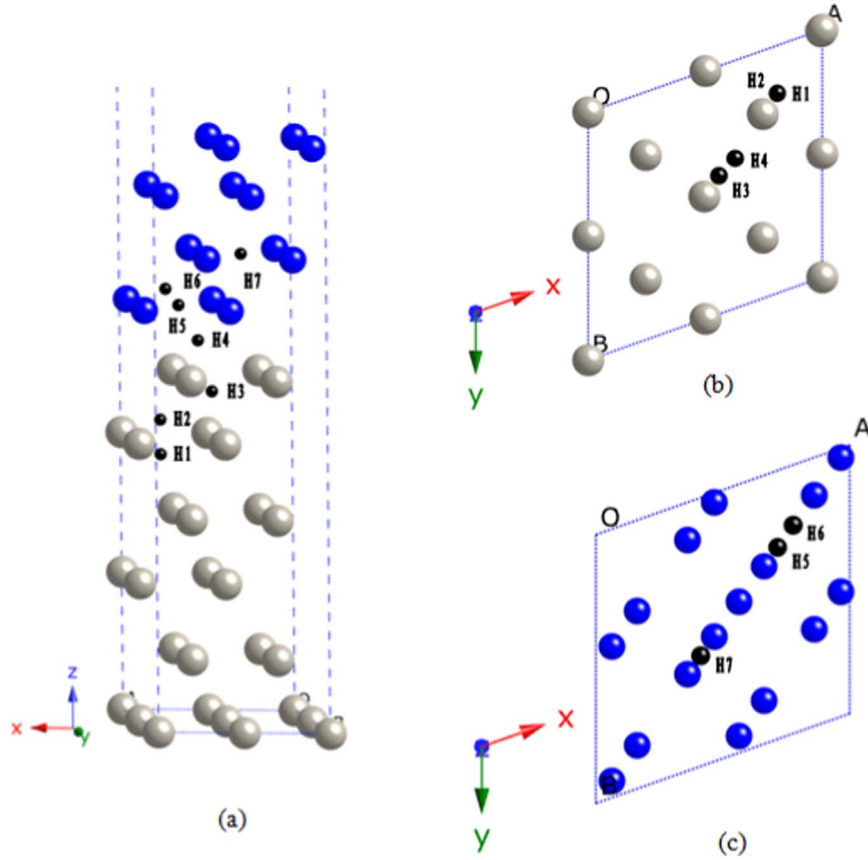


Fig. 1. Schematic illustrations of various interstitial sites (H1~H7) of H atom at the (111)Cu/(110)W interface. (a) is three dimensional model, while (b) and (c) are *x-y* projections of W and Cu lattices, respectively. The big gray, middle blue, and small black balls represent W, Cu, and H atoms, respectively.

properties of Cu/W interface [33–35]. A surface unit cell of 2×2 (4 atoms) with the optimized lattice constant of W bulk ($a = 3.176 \text{ \AA}$) [36] is chosen for each interface model, which has four Cu layers and six W layers with a vacuum distance of 18 \AA . It should be noted that the current interface settings are sufficient to derive reliable cohesion properties of Cu/W interfaces [13,37]. To have a vivid picture of interface structure, Fig. 1 shows the atomic configurations of (111)Cu/(110)W interface, and one H atom is added at octahedral (O) and tetrahedral (T) interstitial sites of the unit cell, which will be shown in detail later.

After the test calculation, the k -meshes of $5 \times 5 \times 1$ and $7 \times 7 \times 1$ are adopted for relaxation and static calculations, respectively. For pure Cu/W interface, the bottom layer of W substrate is fixed, and all other atoms are allowed to fully relax until the forces acting on all W and Cu atoms reach 0.01 meV . Subsequently, one interstitial H atom is added in the above interface for full relaxation. In each calculation, periodic boundary conditions are added in three directions, and the energy criteria are 0.01 and 0.001 meV for relaxation and static calculations, respectively.

The zero-point energy (ZPE) of H is considered in the present study, and is derived through the following formula:

$$E_{ZPE} \approx \frac{1}{2} \sum_j \hbar \omega_j, \quad (1)$$

where ω_j is the frequency associated with the harmonic mode in the gamma point. It should be pointed out that during the calculation of ZPE, the metal atoms of W and Cu are kept fixed and only H atom is relaxed, due to the huge differences of frequencies between H and W or Cu.

In addition, the solution energy (E_{sol}) of H atom is selected to indicate the stability of H atom, and E_{sol} is defined as the energy

released or needed to put H atom at a certain site of the Cu/W interface, i.e., the lower the solution energy, the more stable the H atom at the interface [5]. Moreover, the work of separation (W_{sep}) is used as a parameter to express the interface strength, and W_{sep} is referred as the energy required to reversibly separate the interface into two free surfaces, i.e., a higher W_{sep} signifies a stronger interface cohesion, and vice versa [38].

3. Results and discussion

We first find out possible locations of H atom at the Cu/W interface. As related before, all possible octahedral (O) and tetrahedral (T) interstitial sites of the interface are selected for H atom, and after full relaxation, it is found that H could not stay at some interstitial sites. Fig. 1 shows the seven stable interstitial positions (H1~H7) of H after relaxation, and Table 1 lists the relative coordinates of the seven positions. It should be noted that the H1, H2, and H3 sites are located mainly in the W lattice and could be approximately regarded as the T site, while H5, H6, and H7 are mainly in Cu and close to the O site. Moreover, it can be seen from Fig. 1 that the H4 site is similar to the O site and situated just at the very interface area between W and Cu interface layers.

To investigate the thermodynamic stability of H atom at the Cu/W interface, the solution energy (E_{sol}) of one H atom at various interstitial sites of the Cu/W interface is calculated according to the following formulas [20]:

$$E_{sol} = E_{Cu/W-H} + E_{Cu/W-H}^{ZP} - E_{Cu/W} - \frac{1}{2}E_{H_2} - \frac{1}{2}E_{H_2}^{ZP}, \quad \text{with ZPE} \quad (2)$$

$$E_{sol} = E_{Cu/W-H} - E_{Cu/W} - \frac{1}{2}E_{H_2}, \quad \text{without ZPE} \quad (3)$$

Table 1

Relative coordinates of H atom at various interstitial sites (H1–H7) of the (111)Cu/(110)W interface after relaxation. The three basic vectors of the interface model are (5.501 Å, 0, 0), (−1.834 Å, 5.186 Å, 0), and (0, 0, 38.176 Å) with the three angles of $\alpha=90^\circ$, $\beta=90^\circ$, and $\gamma=109.471^\circ$.

Interstitial site	Relative coordinates of H atom		
	<i>x</i>	<i>y</i>	<i>z</i>
H1	0.807	0.193	0.219
H2	0.807	0.193	0.248
H3	0.556	0.444	0.279
H4	0.625	0.454	0.318
H5	0.715	0.285	0.346
H6	0.784	0.215	0.362
H7	0.472	0.528	0.392

where $E_{\text{Cu/W-H}}$ and $E_{\text{Cu/W}}$ are total energies of the Cu/W interface with and without H atom, respectively, E_{H_2} is total energy of a H_2 molecule, and $E_{\text{H}_2}^{\text{ZPE}}$ and $E_{\text{Cu/W-H}}^{\text{ZPE}}$ are zero-point energies (ZPE) of H_2 molecule and H atom in the Cu/W interface, respectively.

The solution energies (E_{sol}) with and without ZPE are calculated for H atom at various sites (H1–H7) of the Cu/W interface, and the derived values are summarized in Fig. 2. For the sake of comparison, the solution energies of H atom at O and T sites of BCC W and FCC Cu bulks are also obtained and listed in Table 2. During bulk calculations, the supercells of $3\times 3\times 3$ (54 atoms) and $3\times 2\times 2$ (48 atoms) are chosen for BCC W and FCC Cu, respectively. It should be pointed out that the derived ZPE of a H_2 molecule (0.264 eV) from the present study is in good agreement with the corresponding experimental value of 0.268 eV [23].

Several points could be seen from the above calculated values of E_{sol} . Firstly, whether or not ZPE is included as shown in Table 2, the obtained solution energy of H at the T site of W is lower than that of the O site, while H at the O site of Cu is energetically more favorable with smaller E_{sol} than that of the T site. The above comparison indicates that H atom prefers the T site of W and O site of Cu, which match well with similar experimental observations in the literature [39,40]. One can also discern from Table 2 that the derived solution energies of H atom at T site of W and O site of Cu are in good agreement with corresponding values from experiments [40,41]. Such nice agreements suggest that the present PAW-GGA method should be relevant to reflect the intrinsic features of W–H and Cu–H interactions.

Secondly, it can be seen from Fig. 2 and Table 2 that ZPE can increase the solution energy to some extent, while the sequence of the solution energies of H atom at various sites has not been changed due to the addition of ZPE, signifying that ZPE should have a negligible

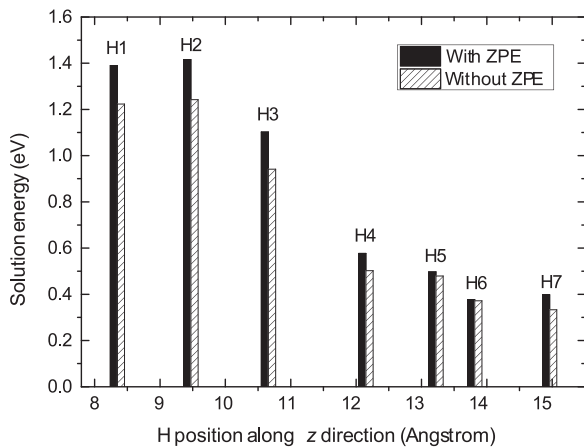


Fig. 2. Solution energy of H atom at various interstitial sites of the (111)Cu/(110)W interface. The bottom layer of the W atoms shown in Fig. 1 is set as the origin of the *z* axis.

Table 2

Solution energies (E_{sol}) of H atom at the T and O sites of BCC W and FCC Cu lattices.

Phase	E_{sol} (eV)		
	Without ZPE	With ZPE	Exp.
WH(T)	0.92	1.05	1.04[39]
WH(O)	1.32	1.34	
CuH(T)	0.63	0.71	0.44[40]
CuH(O)	0.45	0.47	

effect on the relative stability of H atom at various sites. Moreover, one could observe from Table 2 that the derived solution energies of H at T site of W (1.05 eV) with ZPE is in better agreement with the corresponding experimental value of 1.04 eV [39] than that (0.92 eV) without ZPE. All the above features imply that ZPE should be included in the calculation of solution energies of H atom in Cu/W interfaces.

Thirdly, it can be seen from Fig. 2 that the solution energies of H1, H2, and H3 sites from the present calculation are close to the solution energies of H at T and O sites of W bulk. Similarly, the derived E_{sol} values of H at H4, H5, H6, and H7 also approximate the solution energy of H at O site of Cu bulk. Considering that the H1, H2, and H3 sites are mainly within the W lattice and that H5, H6, and H7 are located at the Cu lattice, the above characteristics therefore imply that the interface formation of Cu/W should have only a small effect on solution energy of H. Such small differences between solution energies of H at Cu/W interface and W or Cu bulks would be probably attributed to the variation of W and Cu lattice due to the interface formation.

Fourthly, one could observe clearly from Fig. 2 that the solution energies of H1, H2, and H3 sites are much bigger than those of H4, H5, H6, and H7, suggesting that the location of H should have an important effect on its solution energy, i.e., H atom would energetically prefer Cu lattice or Cu/W interface, instead of W lattice. Note the well-known fact that hydrogen and its isotopes should be abundant in W materials during the process of fusion reactions, a probably useful statement would be given to experimentalists that H atom in the W lattice should have a tendency to diffuse into the Cu/W interface and Cu lattice, in order to reach a lower energy state.

It is of importance to find out the fundamental reason why the location of H has an important effect on its solution energy, and the electronic structures of various H sites are thus calculated and compared with each other. As a typical example, Fig. 3 shows the comparison of total density of states (DOSs) of H atom at H1 and H7 sites of (111)Cu/(110)W interface. One can see obviously from Fig. 3 that the DOSs of H atom at the H7 site are more localized than that at the H1 site, and the heights of the DOS peaks of H at H7 (about 7.0 and 5.5 eV below E_{F}) are much bigger than those at H1. These features of

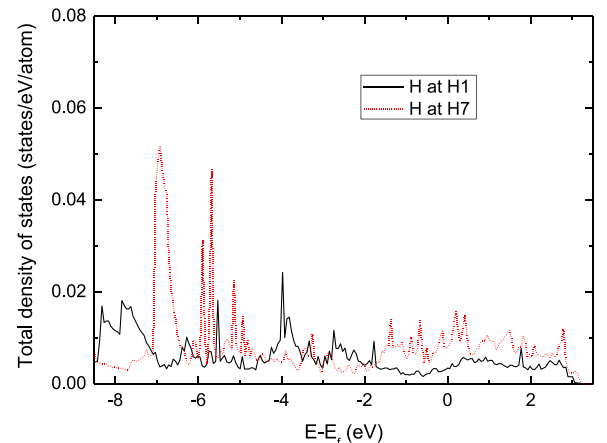


Fig. 3. Comparison of total density of states (DOSs) of H atom at H1 and H7 sites of the (111)Cu/(110)W interface.

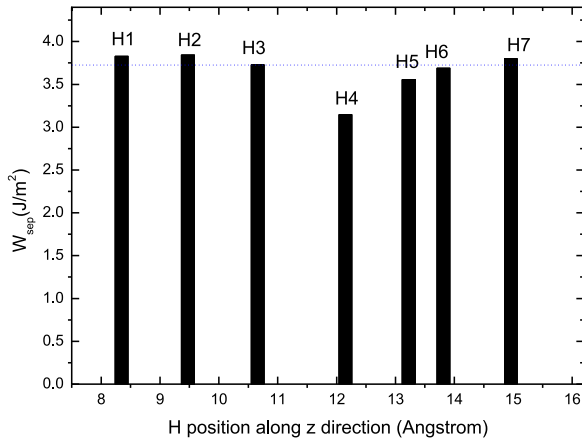


Fig. 4. Work of separation (W_{sep}) of the (111)Cu/(110)W interface with H at various interstitial sites (H1~H7). The W_{sep} (3.773 J/m²) of pure (111)Cu/(110)W interface is shown as a dotted line. The bottom layer of the W atoms shown in Fig. 1 is set as the origin of the z axis.

electronic structures suggest that the chemical bonding of H atom formed at the H7 site should be slightly stronger than that at the H1 site, and such a stronger chemical bonding would therefore bring about the lower solution energy of the H7 site as shown in Fig. 2. It should be noted that H atom could be regarded as an anion at various interstitial sites of Cu/W interface after the calculation of the charge transfer by means of the Bader analysis [42].

We now turn to investigate the effects of interstitial hydrogen on interface strength of the Cu/W interfaces, and the work of separation (W_{sep}) is calculated according to the following formula:

$$W_{sep} = \frac{E_{overlayer} + E_{substrate} - E_{tot}}{A}, \quad (4)$$

where E_{tot} and A are total energy and surface area of the interface, respectively. $E_{overlayer}$ and $E_{substrate}$ are total energies of the overlayer (Cu) and substrate (W) layers after the removal of the substrate and overlayer, respectively. It should be pointed out that H atom at the H4 site is regarded at the W side during the above calculation, as H is closer to W.

The W_{sep} values of (111)Cu/(110)W interface with H at seven interstitial sites of H1~H7 are derived and summarized in Fig. 4. For the sake of comparison, the W_{sep} value (3.773 J/m²) of pure (111)Cu/(110)W interface is also calculated and included in Fig. 4. It can be discerned clearly from Fig. 4 that the W_{sep} value of the H4 site is about 0.63 J/m² lower than that of pure (111)Cu/(110)W interface, whereas the other six sites have W_{sep} values close to pure (111)Cu/(110)W interface. As shown clearly in Fig. 1, the H4 site is just located between the Cu and W interface layers, while the other six sites are within the W or Cu lattices. Considering the above facts together, a beneficial conclusion would be drawn that H atom situated at the very interface area (H4 site) should obviously reduce the interface strength of the Cu/W interface, and that H atom located at the W or Cu lattice has only a small effect on cohesion properties of the Cu/W interface.

Furthermore, we discuss a little bit more about interstitial hydrogen at the Cu/W interface. As related before, H atom in the W lattice has a tendency to diffuse into the Cu/W interface in order to lower its solution energy, and H at the H4 site could dramatically decrease interface strength of the Cu/W interface, which seem hostile to the performance and lifetime of the Cu/W interface. Considering the interfacial location of the H4 site as shown in Fig. 1 and the importance of the Cu/W interface, a probably useful suggestion would be given to experimentalists that possible experimental means should be found to prevent H diffusion into the Cu/W interface, in order to strengthen the cohesion of the Cu/W interface for a longer lifetime.

Finally, it is of interest to obtain the interface dipole formed in the

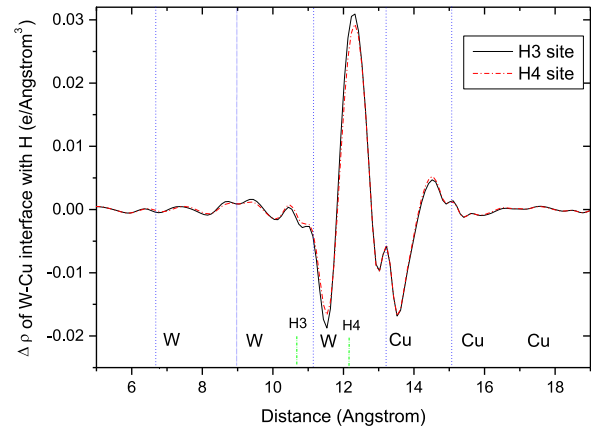


Fig. 5. Charge density change ($\Delta\rho$) along the z direction due to the formation of the (111)Cu/(110)W interface with H at H4 and H3 sites.

Cu/W interface with the addition of interstitial H. As a typical example, Fig. 5 shows the charge density change along the z direction due to the formation of the Cu/W interface with H at the H4 and H3 sites. Several features are evident from the above results. First, interface dipoles are formed in the interface region due to the loss of electrons of both W and Cu atoms. Second, the dipole layers are mainly due to the contributions of interface atoms, and the second layer has only a very small contribution to the interface dipole. Third, the dipole formed in the Cu/W interface with H at the H4 site is slightly smaller than that at the H3 site. Such a difference of interface dipole suggests that a slightly weaker interface bonding has been developed at the H4 site, which would therefore give a deep understanding to the lower interface strength of the H4 site as shown in Fig. 4.

4. Conclusions

Highly accurate first principles calculation has been conducted to investigate the location and stability of hydrogen at the Cu/W interface, and to systematically reveal the influences of hydrogen on interface strength of the Cu/W interface. It is found that the solution energies of H1, H2, and H3 sites are much bigger than those of H4, H5, H6, and H7, suggesting that H atom would energetically prefer the Cu/W interface or Cu lattice, instead of the W lattice. Calculation also reveals that H atom situated at the very interface area (H4 site) could obviously reduce the interface strength of the Cu/W interface, while H atom located at the W or Cu lattice has only a small effect on cohesion properties of the Cu/W interface. The derived results are in good agreement with similar experimental observations in the literature, and are discussed in terms of electronic structures, which could provide a deep understanding to the effects of interstitial hydrogen on cohesion properties of the Cu/W interface.

Acknowledgment

This research work was supported by Key Project of ITER of Ministry of Science and Technology of China (Grant no. 2014GB115000), National Natural Science Foundation of China (Grant no. 51534009), and Project supported by State Key Laboratory of Powder Metallurgy, Central South University, Changsha, China.

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