Difference in formation of hydrogen and helium clusters in tungsten

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The experimentally observed large difference in the depths of hydrogen and helium clusters formed in tungsten still lacks a fundamental explanation. Using density functional theory calculations, molecular dynamics simulations, and kinetic Monte Carlo calculations, we show that the fundamental mechanism behind the different clustering depths is significantly different behaviors of interstitial H and He atoms in W: H–H states are unstable for small interatomic distances whereas He–He states are strongly bound. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2103390]

The properties and behavior of H and He atoms in dense metals are important in several applications, ranging from H storage to H and He embrittlement of materials. Yet many of the basic properties of such systems are not well understood. Of particular importance are the migration properties. These are difficult to measure and quantum mechanical effects like non-Arrhenius migration rates at room or lower temperatures complicate their interpretation both in the bulk[1,2] and at surfaces,[3,4] especially for bcc metals. For example, H and He ions can be implanted into W at so low energies that no lattice damage is produced and the ions stop within the first 100 Å. This situation occurs in the divertor region of fusion reactors and may be the main reason for divertor material erosion. Experiments on W show that even at temperatures where the migration rate of He is larger than for H (at 500 K, for example), He will form bubbles right at the surface, at depths ~100 Å (Ref. 5), while H clusters are formed at micrometer depths.[6–8] Although much studied, the reason to this huge difference is not well established.[6,8]

In this study, we use density-functional theory calculations (DFTC), molecular dynamics simulations (MDS), and kinetic Monte Carlo simulations (KMCS) to show that the difference is explained by the different self-trapping behavior of H and He atoms in W. Helium can trap with other He atoms to form bubble seeds, while the H–H interaction in the W lattice is repulsive at short H–H distances, preventing self-trapping.

The DFTC of H and He energetics in W were performed using the plane wave basis CASTEP code,[9] and implementing the generalized gradient approximation of Perdew and Wang.[10] We used ultrasoft pseudopotentials[11,12] to describe the core electrons. A kinetic energy cutoff of 500 eV was found to converge the energy difference between the studied configurations to within 0.02 eV. The same accuracy was achieved with respect to the k-point sampling of the Brillouin zone. In practice, we used 4 k points, as control runs with 14 points changed our results by less than 0.02 eV.

Slabs with the geometry optimized with the MDS were used as input. The pure system consisted of 54 W atoms in a cubic box. First, the geometry and the box size of the pure system were calculated. Then the formation energies of impurity configurations were computed while keeping the box size fixed. All atoms were fully relaxed until the change in

energy upon ionic displacement was less than 0.02 meV, and the forces less than 0.05 eV/Å.

The energetics of H and He in W was also investigated using MDS. Systems containing 27 648 W atoms and one or two H or He atoms at their respective interstitial sites were relaxed at 0 K and zero pressure. To describe the W–W interaction a potential based on the embedded atom method by Finnis and Sinclair[13] was used. Pair potentials were employed for calculations involving He–He and He–W interactions. The He–He potential was calculated using the DMOL package.[14] For He–W, a new potential developed by us[15] was used. Electronic stopping[16] was applied to all atoms having a kinetic energy higher than or equal to 10 eV. The cutoff radius for all the potentials was 4.4 Å. The MDS for H used new W–W, H–W, and H–H potentials developed at our laboratory.[17]

In order to determine bubble formation depths, KMCS (Refs. 18 and 19) of long time scale defect migration were carried out. Experimentally determined migration prefactors and activation energies for H and He were used.[20,21] The surface area (a square) and the clustering radius (defined later) were the only free parameters. Others, such as temperature, flux and fluence were taken from experimental studies. Surface areas with a border length of 1000 Å were used for the H implantations, whereas border lengths of 2500 and 5000 Å were used for the He implantations. When the distance between two atoms or a cluster and an atom is smaller than the so called clustering distance (or radius), then the two entities are considered to be clustered. We used a clustering distance of 3.16 Å for H and He. We emphasize that these are related to the DFTC and MDS results described later.

To test our DFT and MD interaction models, we first considered single H and He atoms in W. The DFTC and MDS predicted that the interstitial ground state for H is the tetrahedral site, which is in agreement with experiments.[22–25] For He our results are not conclusive on whether the octahedral or tetrahedral site is the stable one. Both DFTC and MDS indicate that these sites are within 0.3 eV of each other, but we do not consider either method accurate enough in this particular case to definitely distinguish which one is the true ground state. However, for the purpose of the present study this is not a significant problem, since (as we describe later) the energy difference between two He atoms near and far from each other is much larger than 0.3 eV.

To understand the possible self-trapping of H and He atoms, we examined the energetics of H and He pairs in W,

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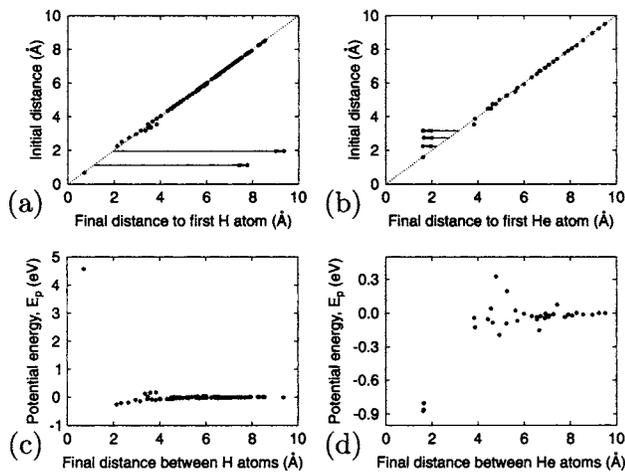
FIG. 1. Initial and final distances between atoms for (a) H–H and (b) He–He in W, as well as potential energy of the (c) H–H and (d) He-He pair in W, as a function of the relaxed distance between the impurity atoms, as predicted by the MDS.

as a function of the distance between the atoms. Two H or He atoms were inserted at interstitial sites and the system was allowed to relax to the nearest energy minimum. The MDS results are shown in Fig. 1. Because of computer capacity limitations we were not able to examine a large number of configurations in the DFTC. We looked only at two in detail, namely the small and large separation (interatomic distance) states.

The results in Fig. 1 show that in the case of two H atoms placed initially at separations of $1-2$ Å, the final distance is very large because the initial configuration is very unstable. This means that the potential energy is at a local maximum or at a point where the potential energy locally is a steep function of the position of the H atoms. The large net force causes the atoms to be repelled, giving them high kinetic energies. This makes the final relaxed distance between the atoms large. After trying several configurations we did manage to keep two H atoms at about the same distance they are in the gas phase, 0.7 Å, but this state is very high in energy.

From Fig. 1(a) it is clear that although the H pair having the smallest interatomic distance seems to be stable, it is practically impossible for two migrating H atoms to come this close to one another, due to the formidable barrier of at least 3 eV (DFTC gave 2.9 eV, MDS 4.9 eV). Both MDS and DFTC indicated the presence of a weakly bound state for two H atoms at a separation of about 2.2 Å, but the binding energy was so low (DFTC gave less than 0.1 eV, MDS gave 0.3 eV) that it can not bind the H atoms for significant times even at room temperature.

Previous studies on H–H interactions in bcc metals have not been conclusive on the nature of the interaction. Analysis of solubility measurements and jellium calculations have indicated that the interaction can be either repulsive or attractive.[26,27] In a review of defect trapping of gas atoms in metals, Picraux[28] discussed self-trapping of H as a possible trapping mechanism without reaching any definite conclusions. Our present result clarifies the situation for W, clearly showing that H self-trapping in W is not possible at room and higher temperatures.

For He we obtained, on the contrary, that the pair having the smallest interatomic distance (about 1.6 Å) is very stable, the binding energy being about 1 eV both in DFTC and MDS. At larger distances both H and He have some fluctuations because different crystal directions give slightly unequal results. We checked with MDS of atom migration that these peaks in potential energy do not constitute a barrier for atomic motion.

These results are counterintuitive because H can form strong covalent bonds with other atoms, while He does not. However, they can be understood based on simple lattice geometry. The He atoms have a high strain field, which is reduced when they are on nearest-neighbor sites. This is shown by a relaxation volume of $\Omega_{He}=9.69$ Å^3 for a single He atom *vs* $\Omega_{He-He}=17.10$ Å^3 for a pair of them, separated by about 3.16 Å, corresponding to a reduction of $\Delta\Omega=2\Omega_{He}-\Omega_{He-He}=2\times9.7$ Å$^3-17.1$ Å$^3=2.28$ Å^3. The corresponding values for H are $\Omega_H=5.269$ Å^3, $\Omega_{H-H}=23.98$ Å^3, and $\Delta\Omega=2\Omega_H-\Omega_{H-H}=-13.6$ Å^3, when the atoms are about 0.7 Å apart. This large expansion of the lattice for the H pair, as compared to two separate H atoms, and the high energy of the H$_2$ dimer, can be understood to be due to the difficulty of inserting the H$_2$ molecule with its cigar-shaped electron structure[29] (due to filling of the bonding orbital of the free molecule) in the bcc lattice.

Already these results provide a qualitative explanation to why He forms clusters close to the surface in W while H does not. We have carried out extensive MDS of He cluster formation[15,30] which show that the self-trapped He$_2$ bound state acts as a seed for further bubble growth. On the contrary, since H cannot form a H$_2$ pair which is stable for significant amounts of time, self-trapping cannot make seeds for H bubble growth.

Next we used KMCS to demonstrate that He atoms implanted into W form clusters at depths similar to those found in experiments. From the DFTC and MDS results, we assume that two He atoms are able to form a bound state when their separation is 3.16 Å or less. This self-trapping distance equals the lattice parameter of W at 0 K. Using He fluxes of $\sim10^{18}$ and $\sim10^{22}$ He m^{-2} s^{-1}, and temperatures of 300 and 2370 K reported in Refs. 5 and 31, we obtain average depths of clustered He atoms of ≈50 Å (trapped by irradiation-induced vacancies) and ≈2300 Å (self-trapped), respectively. A border length of 2500 Å was used for the square implantation surface in the 300 K case. In the high temperature study a border length of 5000 Å was used. The latter cluster depth lies inside the experimental range 0–5000 Å. The former depth is in good agreement with the experimental result of 62 Å. In this 300 K case a damaging ion energy of 1 keV was used in the corresponding experiment.[5] Therefore irradiation-induced vacancies were included as (unsaturable) traps for He atoms. The defect-trapping distance was set equal to the self-trapping distance 3.16 Å.

In addition to the strongly temperature dependent migration rates, also the clustering distance and the jump length (the distance between impurity interstitial sites) used in the KMCS may depend on temperature. We did not take this into account, for the following reasons. The clustering distance has been put to 3.16 Å, which is exactly two times the jump length at 0 K, although a clustering distance closer to ~4 Å could have been used, warranted by Fig. 1(d). The latter value would presumably give rise to even shallower He clusters, but this does not affect the main conclusions reached in this work. The jump length will of course increase with temperature due to thermal expansion, but even at 3000 K the

relative increase in length is less than 2%. Compared to the experimental bubble depth range of 0–5000 Å an uncertainty in the length scale of less than 2% is inconsequential.

In KMCS of H cluster formation in W we first intentionally allowed H atoms to bind with other H atoms, contrary to what the DFTC and MDS indicate. Using a trapping distance of 3.16 Å (equal to the lattice parameter of W at 0 K) and experimental fluxes of 10^{20}, $\sim 10^{22}$, and $\sim 10^{20}$ D m^{-2} s^{-1} and temperatures of 500, 850 and 300 K reported in Refs. 6–8 (all of which used nondamaging atomic ion energies of $\leqslant 1$ keV) we obtained average depths of ~ 100 Å for clustered H atoms. This is orders of magnitude lower than what has been found in the experiments, where the depths are 0.5–10 μm. Clearly, an assumption of self-trapping of H atoms leads to bubble depths quite inconsistent with experiments, and thus supports the conclusion that H self-trapping does not take place, as already indicated by the DFTC and MDS results.

It is clear that H must trap with something in W, since clusters are formed also for nondamaging irradiation.[6–8] Not all defect traps can act as seeds for bubble growth. For instance, using our MDS we found that a single vacancy may bind one or two H atoms but not more. We call traps which can bind several H atoms and thereby act as bubble nucleation centers "multitraps" to distinguish them from traps which can bind only single H atoms.

From various studies a range of natural trap concentrations[32,33] have been obtained. These depend on crystal quality and implantation energies. The traps obtained in these measurements are typically such that they can bind single H atoms, and have quite a high concentration, $\geqslant 10^{24}$ traps m^{-3} (to be compared with the atom density of 6.3×10^{28} W m^{-3}). There are no indications these traps can act as seeds for bubble growth, and KMCS with such high multitrap concentrations lead to bubble formation right at the surface.

Since a reasonably well-defined natural multitrap concentration c_T for H in W is not known, we assume in our KMCS a homogeneous c_T as a free parameter. We found that a multitrap concentration of $\sim 10^{21}$ traps m^{-3} leads to an average bubble depth of ~ 1 μm, which is comparable to the experimental depth values.

In conclusion, using DFT and MD calculations and simulations we have shown that H atoms do not form bound states with other H atoms in the bcc metal W, while He atoms do. Using KMC simulations we showed that this can explain experimental results on why He atoms form bubbles close to the surface in W, while H atoms do not.

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