Molecular dynamics simulations of hydrogen isotope exchange in tungsten vacancies

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ABSTRACT

Solute hydrogen can cause many damaging processes in the lattices of metals, such as deformation of the material, which can take place in large scales through blistering and embrittlement. Especially in nuclear fusion applications, the trapped hydrogen isotope Tritium in the reactor wall materials can pose a radiological safety hazard. Techniques for hydrogen removal from metals usually require high temperatures. However, an efficient low temperature method to remove hydrogen is the so-called *isotope exchange mechanism*, where one isotope is being removed from the material by replacing it by another isotope introduced in the material. The atomic scale exchange mechanism of isotope exchange has not yet been determined. In this study we use molecular dynamics simulations to provide an atomic-scale explanation to the processes related to hydrogen isotope exchange in bulk materials. The results show that the lattice mono-vacancies and small vacancy clusters, usually produced in irradiation experiments, exhibit isotope exchange at low temperatures. The isotope exchange process should also be seen in other hydrogen trapping defects with similar trapping properties as vacancies.

1. Introduction

Due to its high melting point, good thermal properties and low rate of erosion, tungsten (W) has been selected as the divertor armor material for the next-step fusion device ITER and the demonstration fusion power reactor DEMO. Although W experiences relatively low retention of hydrogen isotopes, the constant particle bombardment within a fusion reactor has been shown to increase the trapping of hydrogen by producing open volume defects, such as vacancies. Future fusion reactors will be operated by fusing hydrogen isotopes deuterium (D) and tritium (T) in the form of D-T plasma. Therefore, the trapping of the radioactive H isotope tritium (T) within plasma-facing components can pose a serious safety hazard.

Proposed methods for T removal include thermal treating of the components until most T has been detrapped and removed [1], but also the use of high-power pulsed flashlamps [2] or pulsed lasers [3,4] to only locally heat the material. To successfully remove the major part of the T, however, all the above methods require heating the plasma-facing components to relatively high temperatures for extended periods of time. For example, the ITER plan for T removal consists of vacuum annealing the first wall at 513 K and the divertor at 623 K [5]. Experiments in fuel removal using ITER-relevant temperatures and tokamak samples from the JET ITER-Like Wall project, have shown a removal efficiency of around 40% of the retained hydrogen fuel [1].

The use of hydrogen isotope exchange, a process were heavier trapped hydrogen atoms are released by replacing them with some lighter hydrogen isotope, has, however, been shown to enable annealing at lower temperatures [6]. Other experimental isotope exchange studies in W use hydrogen isotope plasma treatment Experiments on hydrogen isotope exchange has been typically performed by pre-damaged W samples which have been subsequently exposed to D plasmas followed by H exposure for determining the D removal efficiency [7–11]. Results have shown that the D removal by isotope exchange can take place on W surfaces even at 380 K, whereas the bulk effects were observed at 600 K up to depths of $6 \, \mu m$. Previous computational studies have resulted in a hydrogen replacement model introduced in low-Z materials where diffusion is very slow [12] and both simple Rate equation (RE) [13] and 2-D Kinetic Monte Carlo (KMC) models [14] can be used to adequately describe the isotopic exchange on the W surface and in the bulk.

The hydrogen isotope exchange mechanism in W is partly assumed to originate from the interaction of hydrogen with the vacancies. The binding energy of hydrogen to a vacancy depends on the number of hydrogen atoms in the vacancy [15,16]. This fill-level dependency has been recently applied in a RE model to simulate hydrogen isotope exchange in W [17].
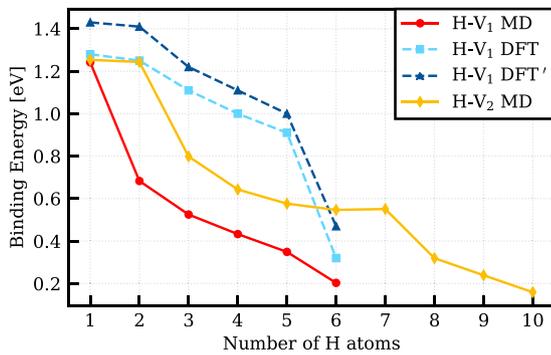

Fig. 1. Comparison of the H–W binding energy in EAM1 by Bonny et al. and DFT results by Heinola et al. [15]. The data set labeled as H–V_1 DFT′ represents the zero-point energy corrected binding energy. There is a clear difference in the DFT and MD binding energies for 2–5 H/Vac. The effect of this binding energy difference to the simulation results are discussed in the results section (Section 3).

Many models utilize simple computational fitting of the experimental results and the actual isotope exchange mechanism is still not certain. In this study, we set out to explore the isotope exchange mechanism on an atomistic scale using molecular dynamics simulations (MD), providing detailed information on the underlying mechanism of the isotope exchange process. We show that the mono-vacancies and small vacancy clusters, usually produced during irradiation experiments, exhibit clear isotope exchange at low temperatures.

2. Simulation methodology

Our modeling of the spontaneous exchange of T with protium (H) was done using MD simulations by employing the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) code [18]. An Embedded Atom Method (EAM) potential for W–H–He systems, referred to as 'EAM1' in [19] was used, due to the potential showing reasonable agreement with *ab initio* data regarding the binding energy in H–vacancy interactions [20], see Fig. 1. The W–W part of the selected potential is based on the much used 'EAM2' potential developed by Marinica et al. [21] and known for providing elastic constants and point defect properties in good agreement with both experiments and Density Functional Theory (DFT) calculations [22].

For all production run MD simulations, a $32 \times 32 \times 32$ Å^3 simulation cell containing 2000 W atoms of bulk W was used. Periodic boundaries were applied in all directions and a Nosé–Hoover thermostat was used to approximate a canonical ensemble, emulating the heat bath formed by the surrounding lattice.

The number of hydrogen atoms in a W mono-vacancy at around room temperature has been shown to be five [15]. In order to generate the mono-vacancy system, the atom closest to the center of the simulation cell is removed and six T atoms are added around the produced point defect to fully saturate it. An additional 20 H atoms were distributed randomly in tetrahedral interstitial positions around the lattice, bringing the total H/W ratio to 1.3%. After this initialization, the system is relaxed using the built-in conjugate gradient energy minimization function in LAMMPS.

After the relaxation phase, the actual simulation run was performed in intervals of 5 ps, until all of the T atoms were observed to be detrapped from the mono-vacancy. Depending on the temperature, this results to a total simulation time of 300...1500 ns. The free and mobile T atoms, which had diffused across the periodic boundaries, were removed from the system between each successive simulation interval to avoid artificial re-trapping processes and to emulate the diffusion process over long distances.

Because of the long simulation times, accumulated floating point errors might result in numerical integration artifacts such as the 'flying
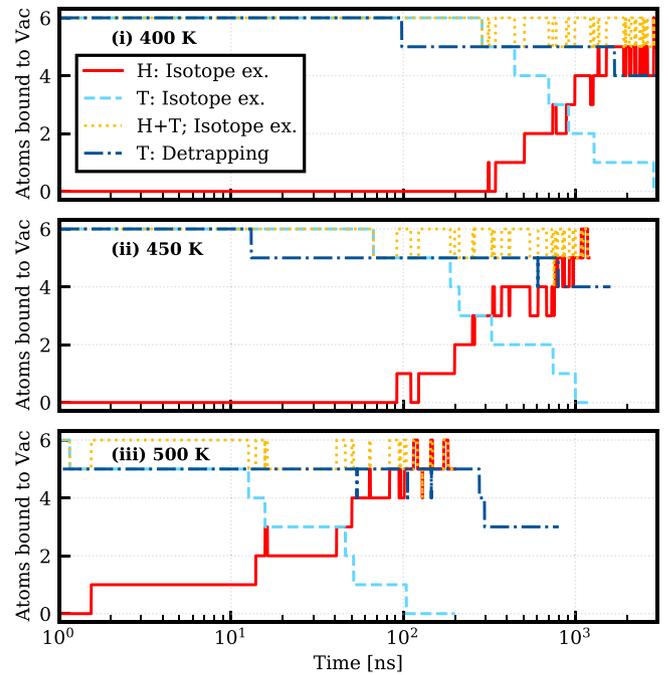

Fig. 2. Number of H and T in the monovacancy as function of time at 400, 450 and 500 K.

ice cube', i.e. unphysical accelerated center-of-mass motion (COM) across periodic boundaries. To prevent this, the COM velocity is removed every 10 000 time steps without affecting relative velocities of atoms.

Finally, the T removal rate was determined by studying the number of hydrogen atoms bound to the mono-vacancy as a function of time. For simplicity, atoms were considered to be bound to the vacancy if they were found within a cubic region of side length 4 Å, centered around the mono-vacancy.

In order to verify that neither the selected simulation system dimensions nor the initial atom velocities affected the results, two individual comparison simulations, yielding qualitatively identical results, were performed using a 5488 and a 14 858 W atom system, with the same hydrogen concentration, but unique random seeds used for velocity generation and H atom placement. The 14 858 W atom comparison system was constructed with the cell dimensions chosen as the prime triplet $17 \times 19 \times 23$ Å^3 to additionally rule out any artificial effects due to a highly symmetrical simulation cell.

3. Results and discussion

In simulations at 500 K (Fig. 2), the tritium was completely exchanged with protium during the first 100 ns. Simulations at temperatures of 450 and 400 K also show a complete isotope exchange, but the required time for full isotope exchange to take place increased to about 1000 ns and 3000 ns, respectively. The position of the vacancy site remained unchanged during all performed simulations.

Reference simulations without any added H atoms were run at 400 K, 450 K and 500 K, with T being removed simply due to detrapping and diffusion. The results of these simulations, shown in Fig. 2, indicate a significant decrease in the T removal efficiency compared to when isotope exchange is taking place. At all considered temperatures, the tritium removal is significantly faster in the systems with H atoms present. The qualitatively identical results of the single comparison simulation with a 14 858 W atom system are provided in Fig. 3 for reference.
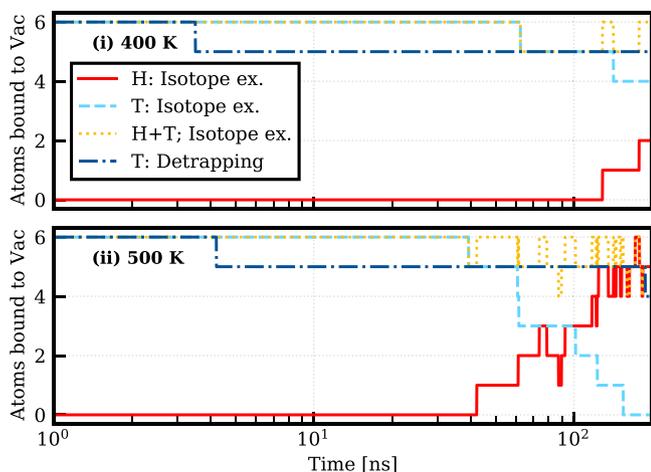
Fig. 3. A comparison between detrapping (vacuum annealing) and isotope exchange in a larger, 14 858 W atom system.

This conclusion stands even though the MD potential yields smaller binding energy values for the hydrogen–vacancy interaction than DFT in the case of 2–5 H/Vac.

As one can conclude from the DFT binding energy values shown in Fig. 1, annealing at and below 500 K would only result in the detrapping of the sixth and loosest bound T atom and the remaining five T would subsequently have very low probabilities of becoming detrapped. In Fig. 2, however, we see that in the H-free system, about 2 to 3 T are detrapped from the vacancy, which is a result of the too low H–Vac binding energies in MD.

How would the current simulation results then change if the binding energies for the potential would be roughly the same as for DFT? Firstly, there would likely be no less than five T bound to the mono-vacancy in the mono-isotopic case, due to the relatively high binding energy of the fifth T (ca 0.9 eV). Secondly, the effect on the isotope exchange results would be minor, since, as seen in Fig. 2, the combined amount of H and T in the mono-vacancy remains as five or six in all the simulations. This means that only the sixth hydrogen atom is always detrapped and before any additional detrapping has occurred, a H (or T) atom has been trapped in its place. Thus, an increase in the binding energies of the five first hydrogen atoms to the mono-vacancy should have no or only minor effects on the obtained results.

Since the hydrogen atom is a light-mass particle, the quantum-mechanical vibration effects on the binding energies are not negligible. Fig. 1 shows the zero-point energy (ZPE) corrected binding energies for hydrogen, determined using DFT. These quantum-mechanical vibration effects are not taken into account in the MD method. The effect of the ZPE corrected, slightly larger binding energy, on the obtained results would be minor. As concluded earlier, an increase in the binding energies of the five first hydrogen atoms do not alter the qualitative isotope effect results, and the ZPE corrected binding energy of the sixth hydrogen atom is still small enough for detrapping to occur at these temperatures.

The underlying mechanism for isotope exchange can be understood by examining fluctuations in the activation energy, i.e. the energy difference between potential energy of an individual H atom and the saddle point of the trapping barrier. In Fig. 4, we see that the activation energy fluctuates rapidly, due to potential energy changes associated with the atoms shifting slightly around the defect. A hydrogen atom, trapped in the vacancy as the sixth and most loosely bound atom, constantly and very rapidly exchanges positions and energies with the other trapped hydrogen atoms. Therefore, any one of the six hydrogen atoms is detrapped with almost equal probability, regardless of its isotope or the order in which it has been trapped the vacancy. The
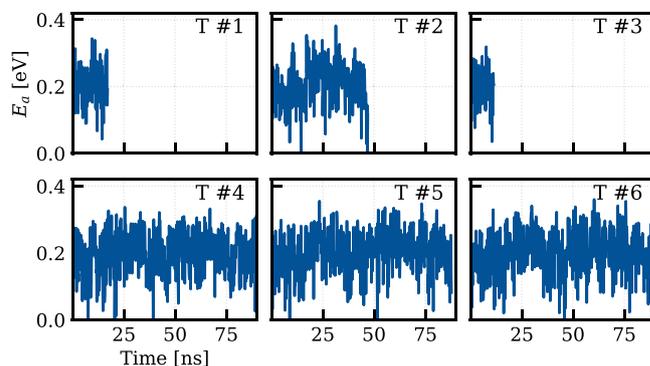

Fig. 4. The activation energies of the individual T atoms in a 500 K simulation plotted as functions of time. A lower value indicates less additional energy required for detrapping.
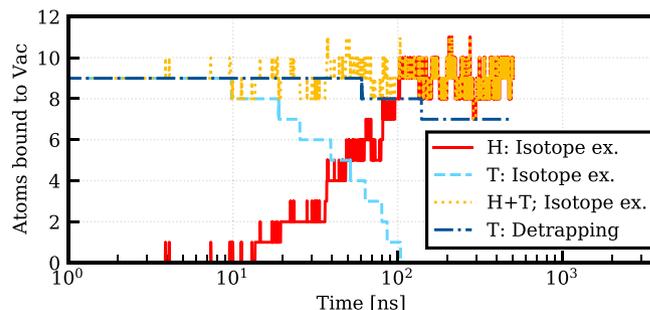

Fig. 5. A comparison between detrapping (vacuum annealing) and isotope exchange in a di-vacancy system.

detrapping probability, however, still depends on the jump frequency ($\propto 1/\sqrt{mass}$) and zero-point energy difference. As a conclusion, the isotope exchange mechanism is seen in all defects where the hydrogen atoms can fast exchange positions and binding energies.

For most simulations a H/W ratio of 1.3% (20 H + 6 T + 2000 W) was used, however similar trends could be seen also using ratios of 0.5%. For additional comparison, isotope exchange was also simulated briefly in a di-vacancy system at 500 K. The system, while otherwise identical to that used for mono-vacancies, had two vacancies introduced at adjacent lattice sites, with a total of 10 T atoms bound to the defect. These results are shown in Fig. 5.

4. Conclusions

Being well in line with earlier experimental work in the field [6], our results provide an atom-level view into the isotope exchange mechanism, showing that it indeed is based on keeping the defect saturated, with loosely bound hydrogen atoms available through the entire removal process. Our results indicate significantly improved tritium removal rates for all considered temperatures when isotope exchange is employed, compared to pure one isotope detrapping removal by annealing.

Finally, our results serve to prove that it is possible to study the mechanism of isotope exchange using molecular dynamics methods, despite the inherent limitations on simulation time scales and system sizes. With simulation times ranging up to microseconds and a temporal resolution of the order of picoseconds, MD provides an excellent tool for bridging the gap between micro- and macroscopic studies.

The isotope exchange process should also apply to other defects, mainly grain boundaries and dislocations, where hydrogen is trapped and can change position and binding energy states. However, the exchange process might be slower if the distance between the core of the

defect, where the binding energy is higher, and the defect boundary, where it is lower, is large. In this case, the atomic interchange between the strongly bound and the recently trapped, loosely bound isotopes, is slow.

CRediT authorship contribution statement

O. Lindblom: Software, Formal analysis, Data curation, Visualization, Writing – original draft. **T. Ahlgren:** Conceptualization, Methodology, Project administration. **K. Heinola:** Writing – review & editing, Supervision, Funding acquisition, Validation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

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