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Concentration dependent hydrogen diffusion in tungsten

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HIGHLIGHTS

- The recommended value of 0.39 eV for the H in W migration barrier should be changed to 0.25 eV.
- The random oscillation of atoms around the equilibrium position can be dealt with in diffusion simulations.
- Hydrogen diffusion in tungsten is highly concentration dependent.

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ABSTRACT

The diffusion of hydrogen in tungsten is studied as a function of temperature, hydrogen concentration and pressure using Molecular Dynamics technique. A new analysis method to determine diffusion coefficients that accounts for the random oscillation of atoms around the equilibrium position is presented. The results indicate that the hydrogen migration barrier of 0.25 eV should be used instead of the presently recommended value of 0.39 eV. This conclusion is supported by both experiments and density functional theory calculations. Moreover, the migration volume at the saddle point for H in W is found to be positive: $\Delta V_m \approx 0.488$ Å^3, leading to a decrease in the diffusivity at high pressures. At high H concentrations, a dramatic reduction in the diffusion coefficient is observed, due to site blocking and the repulsive H-H interaction. The results of this study indicates that high flux hydrogen irradiation leads to much higher H concentrations in tungsten than expected.

1. Introduction

Tungsten (W) is one of the strongest candidates to be used as the divertor plate material for the next step fusion device (ITER) due to its high melting point, low erosion rate, good thermal conductivity and low hydrogen retention. Such combination of properties makes W a promising plasma-facing wall material. However, continuous bombardment with low energy hydrogen isotopes is seen to introduce defects in plasma facing materials. Open volume defects, such as vacancies, are known to trap hydrogen (H) and thus are the main reasons for H retention in W. In fusion reactors this is a critical issue due to the tritium retention.

The presence of H strongly affects most of the W properties, due to phenomena like vacancy formation and blistering [1,2]. Moreover, H is known to be trapped in impurities, vacancies, dislocations and grain boundaries [3–5], affecting the micro-structure evolution of the material. In order to be able to predict and calculate the evolution of the micro-structure, tritium retention, and other thermal and mechanical properties, it is essential to know the H concentration present in the material.

The H atom is an endothermic impurity in W with a solution energy E_{sol} of about 1 eV [6]. This means that the equilibrium H concentration $C_{H,eq}$ in W is very low unless a large H_2 pressure (P) is present at the W surface at high temperature (T); $C_{H,eq} \propto \sqrt{(P)} exp(-(E_{sol} - T\Delta S)/k_B T)$, where ΔS is the entropy change and k_B is the Boltzmann constant. However, large H flux from a fusion device, plasma source or ion implanter can result in concentrations that considerably exceeds equilibrium value in W. This H concentration is proportional to the incoming flux and inverse proportional to the H diffusivity. The H diffusivity, however, is a function of the concentration itself. At high concentrations, the diffusivity should decrease due to the adjacent interstitial site blocking [7], and due to the short-range H-H repulsion [8,9]. Hence, the decreasing diffusivity will increase the

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concentration, affecting the properties of the W material. To our knowledge, no data on concentration dependent H diffusion in W is found in the literature.

In this study, using molecular dynamics simulations we derive equations showing H diffusion coefficient dependence on the H concentration. We present a new analysis method to determine diffusion coefficients that accounts for the random oscillation of atoms around the equilibrium position. Moreover, we review the H diffusion coefficient at low concentrations in W, and suggest that the commonly used H diffusion parameters should be revised.

2. Computational method

Our modelling of H diffusion in W is done employing molecular dynamics simulations (MD) [10] using the bond-order potential by Li et al. [11] to describe the forces between W-W, W-H and H-H atoms. We use the Berendsen thermostat to control the atom velocity distribution, which for large systems of over hundreds of atoms approximately generates a correct canonical ensemble. Since the timestep is proportional to $M^{-1/2}$ [10], where M is the atom mass, heavy hydrogen isotope deuterium (D) is chosen to improve the efficiency of MD simulations. The results are easily scaled with square the root of the atomic mass of D to obtain the diffusion coefficient of H [12,13].

Depending on the D concentration two different W simulation cell sizes are used. For high D concentrations we use a 6 × 6 × 6, 432 W atom system. We have checked the validity of the 6 × 6 × 6 system size by performing the simulations in the low limit D concentration case (1 D atom in the system) also with a 10 × 10 × 10 cell containing 2000 W atoms. The system size does not affect the resulting diffusion coefficients. To track the actual D position during the MD simulations, also positions omitting the periodic boundary conditions were saved. The pressure during simulation is kept constant at 0 kbar. Temperatures lower than 300 K are not investigated due to the limitations of the MD simulation time scale, besides, at T below 300 K quantum tunneling starts to dominate [14,15].

To determine the diffusion coefficient, we need the atomic positions at different simulation times. How often the positions can be saved is bounded by the data storage capacity. However, if the positions are saved too seldom, the error in calculating the diffusion coefficient increases, see section 3. To optimize the simulations, we counted the number of atomic diffusion jumps as a function of the saving time interval. The 3D diffusion coefficient in cubic lattices can be written as: $D = 1/6 \cdot \lambda^2 \cdot \Gamma$, where λ is the diffusion jump length and Γ is the jump frequency. The mean residence time the diffusing atom spends at each site becomes: $T_{res} = 1/\Gamma = \lambda^2/(6D)$. In Table 1 we see that saving the position about hundred times more often than the mean time between diffusion jumps (0.01 T_{res}), as is done in this study, records about 99.2% of all the diffusion jumps.

Table 1
The percentage of the counted atomic diffusion jumps in the simulation as a function of the saving time interval.

Times Δ saving time (T_{res})	Number of jumps saved
1000	0.01%
100	1.00%
10	9.66%
1	58.45%
0.1	94.04%
0.01	99.19%

3. Results and discussion

3.1. Diffusion coefficient at low concentrations

The simulation of D diffusion coefficient for low D concentration (D/W = 1/2000) is done in the temperature range between 300 and 1500 K, and diffusion times between 1 and 20 ns. The D position during simulation is tracked using the Wigner-Seitz cell analysis, where the closest tetrahedral interstitial site (TIS) is found and is assigned to be the D position in the diffusion coefficient analysis. Fig. 1 illustrates the real X-position of the D atom, and the one used in the analysis as a function of the simulation time. The deuterium diffusion coefficient is determined by the Einstein-Smoluchowsky equation using the independent interval method (IIM) [16], as follows:

$$D = \frac{1}{6N}\frac{\sum_i^N \Delta R_i^2}{\sum_i^N \Delta T}, \tag{1}$$

where ΔR_i^2 is the square displacement of the diffusing atom, ΔT_i – the diffusion time and N – the number of intervals the path is divided into. The diffusion coefficient can further be written as the Arrhenius function of the pre-exponential factor D_0 and migration barrier E_m

$$D = D_0 exp\left(-\frac{E_m}{k_B T}\right), \tag{2}$$

where T is the absolute temperature and k_B the Boltzmann constant. The diffusion parameters from this study and found in the literature are presented in Table 2.

The currently accepted and recommended [20] migration barrier of 0.39 eV for hydrogen is from Fraunfelder experiments [6]. Table 2 and Fig. 2 show that if the Arrhenius fit to Fraunfelder data is done omitting the two lowest temperature points (less than 1400 K), the migration barrier results in value of 0.25 eV. This value is consistent with the present study, the DFT study by Heinola et al. [18] and the experimental permiation study by Nemanic et al. [19]. The Fraunfelder data has been divided by the square root of the D atomic mass to account for the isotope effect on diffusion pre-exponential factor [12,13].

The two lowest temperature Fraunfelder diffusion coefficients

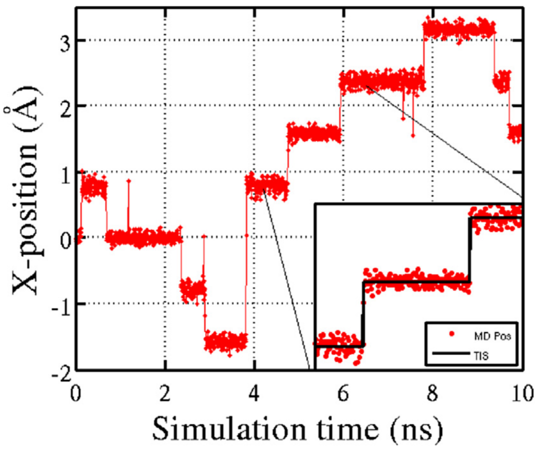

Fig. 1. Example of the D atom X-position during the 300 K MD simulation. The random oscillation around the tetrahedral interstitial site (TIS) is eliminated using the Wigner-Seitz cell analysis, giving a more accurate diffusion coefficient.