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Modeling of hydrogen desorption from tungsten surface

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ABSTRACT

Hydrogen retention in metallic plasma-facing components is among key-issues for future fusion devices. For tungsten, which has been chosen as divertor material in ITER, hydrogen desorption parameters experimentally measured for fusion-related conditions show large discrepancies. In this paper, we therefore investigate hydrogen recombination and desorption on tungsten surfaces using molecular dynamics simulations and accelerated molecular dynamics simulations to analyze adsorption states, diffusion, hydrogen recombination into molecules, and clustering of hydrogen on tungsten surfaces. The quality of tungsten hydrogen interatomic potential is discussed in the light of MD simulations results, showing that three body interactions in current interatomic potential do not allow to reproduce hydrogen molecular recombination and desorption. Effects of surface hydrogen clustering on hydrogen desorption are analyzed by introducing a kinetic model describing the competition between surface diffusion, clustering and recombination. Different desorption regimes are identified and reproduce some aspects of desorption regimes experimentally observed.

1. Introduction

Hydrogen retention and recycling from plasma facing components (PFCs) are among key issues for future fusion devices. In ITER, tungsten divertor will be exposed to high flux of hydrogen isotopes during long term operations ($\Gamma_D \approx 10^{24}\,\mathrm{m}^{-2}\,\mathrm{s}^{-1}$, $t_{\mathrm{exposure}} \sim 500\,\mathrm{s}$), resulting in long-term hydrogen retention in tungsten components. Understanding mechanisms of hydrogen retention in tungsten is then crucial for safety reasons and due to synergistic effects between plasma and PFCs during plasma operations [1].

Large time and space scales relevant for retention in fusion reactor conditions impose to model retention in PFCs with reaction–diffusion equations, for which boundary conditions are determined by surface processes. In this context, hydrogen desorption from tungsten surface is usually described as desorption of hydrogen molecules formed by recombination of adsorbed hydrogen atoms on surface. Hydrogen desorption flux is then described as corresponding to a second-order kinetic process (1).

$$\Gamma_{\mathrm{des}} = \underbrace{K_0 e^{-\frac{E_{\mathrm{des}}}{T}}}_{K_r} c_s^2 \tag{1}$$

However, experimental data show large discrepancies for K_0 and E_{des} and contradictory temperature dependencies of K_r [1]. In addition, several binding states for adsorbed hydrogen on tungsten surface were observed in thermodesorption experiments and desorption kinetic order may be different from two [2]. Desorption parameters (E_{des}, K_0) also vary significantly when hydrogen surface coverage exceeds 0.5 [3].

These experimental results suggest that some complex surface processes might be not well described by (1) and remain not well understood. However, these surface processes may play an important role when hydrogen coverage of tungsten surface is high, as it is expected for long term exposure of tungsten components to high flux of hydrogen at low temperature ($T < 900\,\mathrm{K}$), e.g. in ITER scenarii or in thermodesorption experiments. Modeling hydrogen desorption mechanisms is thus required to predict hydrogen retention in tungsten irradiated with high doses of hydrogen.

Analyzing hydrogen desorption from tungsten surface using macroscopic models with reaction–diffusion equations is difficult due to large discrepancies in surface reactions parameters (E_r, K_0) kinetic order of desorption). In this paper, we therefore propose to investigate atomic processes governing surface desorption from tungsten using molecular dynamics simulations (MD) and accelerated molecular dynamics simulations (AMD).

MD simulations were performed using W–H Tersoff interatomic potential proposed in [8]. Due to high computational costs induced

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by Tersoff type potential, only temperature accelerated dynamics (TAD) was used as AMD method [4].

We focus in this paper on hydrogen desorption from clean and flat tungsten ⟨100⟩ and ⟨110⟩ surfaces. In the first part of this paper, we characterize hydrogen adsorption sites on ⟨100⟩ tungsten surfaces and TAD is used to analyze hydrogen diffusion on surface. Hydrogen desorption from tungsten surfaces is then investigated at high temperature and analysis of interatomic potential parameters affecting desorption is provided. In the last part, we examine diffusion of hydrogen on tungsten surfaces at high coverage and low temperature, for which hydrogen clustering is observed on tungsten surfaces. Clustering process is modeled and its effects on desorption are discussed.

2. Hydrogen adsorption states and diffusion paths on tungsten surfaces

In MD and AMD simulations, tungsten surfaces were normal to the z-direction and the simulation box was periodic in x and y directions. Upper surfaces at $z = 0$ were kept as free surface, while the four last layers forming the opposite surface were frozen. The MD time step was set to 0.1 fs.

To analyze hydrogen adsorption sites on tungsten surface, sampling of potential energy of interaction $U_{\mathrm{H-W}} < 0$ between a single hydrogen atom and tungsten surface, which lies at $z = z_0$, was performed by slowly moving the hydrogen atom toward W surface in z-direction for several x and y positions. Tungsten surface was maintained at temperature lower than 0.1 K by an external viscous force. Binding energy $E_b(x, y) = \max_{z_0<z<+\infty}(-U_{\mathrm{H-W}})$ of hydrogen adsorbed on ⟨100⟩ W surface, mapped in x and y directions, show several adsorption sites with different adsorption energy $E_{\mathrm{ads}} = E_b$ (Fig. 1): the bridge site (B) ($E_{\mathrm{ads}} = 2.39$ eV), the threefold hollow site (T) ($E_{\mathrm{ads}} = 2.35$ eV), the orthohedral site (O) ($E_{\mathrm{ads}} = 2.4$ eV) and several narrow sites (D) ($E_{\mathrm{ads}} = 1.9$ eV).

E_{ads} for (B) sites on ⟨100⟩ surface is close to E_{ads} found with LEPS potential (2.40 eV) [5] and in agreement, regarding experimental uncertainties, with experimental values of the activation energy $E_{\mathrm{des,H}}$ for hydrogen desorption as single atom from polycrystalline tungsten ($E_{\mathrm{des,H}} \approx 2.91$ eV [6]). Moreover, H_2 molecules have been experimentally observed dissociating on tungsten surface into adsorbed atoms in bridge sites [6], and dissociation of H_2 on tungsten surface is known to be exothermic, which is satisfied by adsorption energies found on ⟨100⟩ surface $\left(E_{\mathrm{ads}} < \frac{E_{\mathrm{H_2}}}{2} \approx 2.26\ \mathrm{eV}\right)$.

Activation energies of hydrogen transition (migration) between adsorption sites are needed to characterize hydrogen diffusion on tungsten surface, but cannot be determined with E_b map (Fig. 1) since free hydrogen motion in x and y directions is necessary to characterize transition paths between adsorption sites. TAD simulations with one hydrogen atom on tungsten surface were then used to analyze hydrogen transitions between adsorption sites, and to estimate activation energy of these transitions with the nudged elastic band method (NEB [7]). Using low temperature equal to 500 K and high temperature equal to 1200 K, TAD have been performed on ⟨100⟩ surfaces, revealing one additional adsorption site (T2) with $E_{\mathrm{ads}} \approx 2.15$ eV, in addition to other sites previously found (Fig. 2).

Activation energy of hydrogen transition between adsorption sites estimated with NEB method, plotted in Fig. 2, show that the transition (T) → (B) has the highest activation energy ($E_{\mathrm{(T)\to(B)}}$ - ≈ 0.55 eV), while reciprocal transition shows $E_{\mathrm{(B)\to(T)}} \approx 0.35$ eV. Activation energies for other transitions do not exceed 0.35 eV and are weak for (D) → (T2) ($E_{\mathrm{(D)\to(T2)}} < 0.1$ eV). Transitions between adsorption sites occur only between spatially adjacent states, and hydrogen atoms can thus only migrate from one lattice cell to an adjacent one through (B) sites. It suggests that the diffusion of hydrogen on ⟨100⟩ surface is limited by hydrogen migration from (T) to (B) sites, and that the activation energy for diffusion E_{D} is determined by $E_{\mathrm{D}} \approx E_{\mathrm{(T)\to(B)}} \approx 0.55$ eV.

However, transition barriers between adsorption sites other than (B) sites are lower than barriers for transitions toward (B) sites, and therefore hydrogen atoms will mostly explore sites (T, T2, O, D) before exploring (B) sites. Since transition barrier to (D) sites are low, hydrogen easily migrate from (T) to (D), which tends to complicate effective adsorption potential structure in lattice cells, and eventually affect hydrogen migration between lattice cells. Quantitative estimations of the residency time of hydrogen atom in each adsorption sites during TAD simulations show that hydrogen atom indeed mostly occupies (T, T2, D) sites $\left(t^{\mathrm{(T,T2,D,0)}}_{\mathrm{residency}} \sim 10^{-7}\ \mathrm{s}\right)$ and rarely visits (B) sites $\left(t^{\mathrm{(B)}}_{\mathrm{residency}} \sim 10^{-9}\ \mathrm{s}\right)$.

These observations suggest that diffusion process of hydrogen atom on ⟨100⟩ surface might be more complex than diffusion modeled by single hydrogen hop from one lattice cell to another

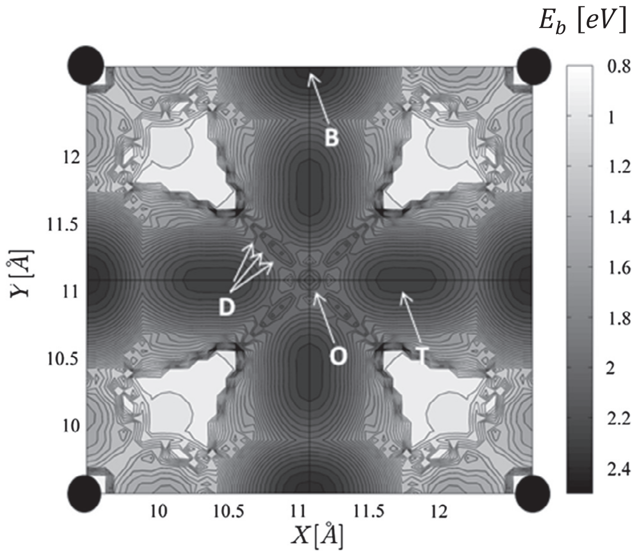

Fig. 1. Hydrogen binding energy $E_b(x, y)$ on ⟨100⟩ tungsten surface. Several adsorptions sites can be identified (B, T, O, D). Black circles represent tungsten surface atoms for surface without hydrogen.

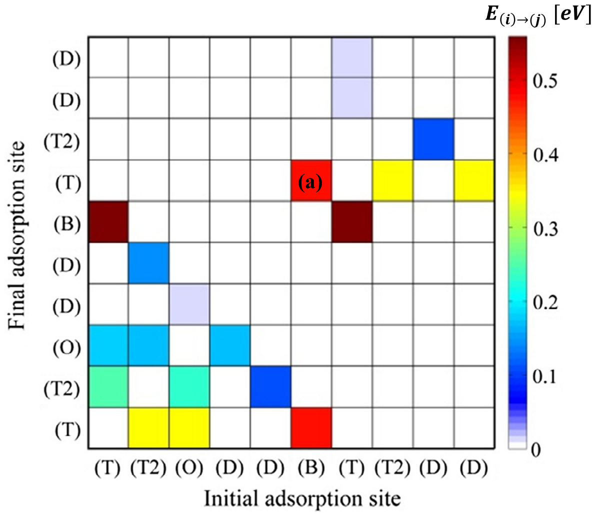

Fig. 2. Activation energy $E_{(i)\to(j)}$ of transition between adsorption states (i) and (j) on ⟨100⟩ surface estimated with NEB method. E.g. transition (a) corresponds to the transition from (B) site to (T) site with $E_{\mathrm{(B)\to(T)}} = 0.48$ eV.

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