Temperature dependence of D atom adsorption on polycrystalline tungsten

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ABSTRACT

Temperature dependence of D atom adsorption on polycrystalline tungsten was studied by *in situ* ion beam method Elastic Recoil Detection Analysis (ERDA). A new procedure named thermoadsorption (TA) was developed for this study, where the sample is first exposed to a deuterium atom beam at high temperature and then, while being continuously exposed to the atom beam, is slowly cooled down. H and D concentrations are determined during this cooling by ERDA. A stepwise increase of the surface areal density was observed starting from $(1.2 \pm 0.3) \times 10^{15}$ D cm^{-2} at sample temperature around 750 K, to $(2.2 \pm 0.3) \times 10^{15}$ D cm^{-2} when temperature was around 600–500 K and final increase to $(6.8 \pm 0.6) \times 10^{15}$ D cm^{-2} when sample temperature was below 440 K. From this, three individual binding states were identified for the studied polycrystalline tungsten. We present a numerical model adequate to our experimental procedure which was developed by taking into account all relevant surface processes. The binding energies for desorption/adsorption were derived by modeling the TA data with the numerical model and were determined to be: 1.05 ± 0.06 eV, 1.7 ± 0.08 eV and >2.2 eV. Isotope exchange at 485 K sample temperature was also measured and modeled. An estimate of the reflection coefficient for 0.2 eV hydrogen atoms on polycrystalline W was obtained from modeling the isotope exchange data and was determined to be 0.96 ± 0.02.

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1. Introduction

Studies of hydrogen interaction with surfaces represent an extensive and very active research activity due to the fundamental nature of the subject, hydrogen atoms or molecules being the simplest adsorbing species, and on the other hand due to the large number of hydrogen related applications (fusion, hydrogen fuel cells, plasma processing, etc.). Main interest in this paper is the hydrogen interaction with tungsten. One can find in the literature extensive experimental [1–7] and theoretical [8–12] studies on hydrogen molecule interaction with tungsten but only few studies were done with hydrogen atoms [11]. With atoms an additional process comes into play which is not possible with molecules, i.e. Eley–Rideal type atom recombination described in more detail below. For hydrogen on tungsten reactions on the surface are expected to be dominant, since it has a positive heat of solubility and therefore diffusion of hydrogen atoms from the surface in the bulk is small

[13]. A polycrystalline tungsten surface consists predominantly of (1 1 0), (1 1 1) and (1 0 0) surfaces [2]. The saturation surface density obtained from the thermodesorption (TD) study [2] for these single-crystal surfaces is 1.05×10^{15} H cm^{-2} (0.74 monolayer (ML)), 2.6×10^{15} H cm^{-2} (4.5 ML) and 1.5×10^{15} H cm^{-2} (1.5 ML) for W(1 1 0), W(1 1 1) and W(1 0 0), respectively. Several binding states were found to exist on these single crystal W surfaces, each having a characteristic desorption energy E_{des} [2]. These surface properties are not known for polycrystalline tungsten but on the other hand can influence hydrogen adsorption and reemission. Namely, hydrogen molecule production by atom recombination on the surface, especially vibrational excitation of the molecules, is influenced among others by the properties of the surface adsorption sites [14,15].

The interest in the hydrogen interaction with tungsten has increased recently, since tungsten is a material of choice for the target plates in the divertor of modern fusion devices, tokamaks [16,17]. In the divertor, the bottom part of the tokamak, plasma is intentionally directed to the target plates [16] which are therefore subjected to high particle fluxes and heat loads. The prediction of hydrogen retention in W is an important issue especially due to the safety limitations on the total amount of the hydrogen isotope

tritium in the reactor. Therefore, the control of the in-vessel tritium inventory is of high importance [17]. The deuterium retention in W exposed to low-energy deuterium plasma and ion beams has been studied and theoretically supported [18–24]. Thermodesorption spectroscopy (TDS) and nuclear reaction analysis (NRA), using the $D(^3He,p)^4He$ nuclear reaction, are commonly used techniques for determination of the binding/trapping sites and hydrogenic retention after material exposure to plasma or ion beams. There was no study of retention and isotopic exchange in W exposed to low energy (< eV) atoms. It is very important from the fundamental point of view to understand the hydrogen isotope migration and retention in W since thermal atoms are expected not to produce additional damage in the material but only decorate the existing trapping sites.

Here we report on the first detailed study of low energy (0.2 eV) hydrogen/deuterium atom interaction on polycrystalline (PC) tungsten as a function of the sample temperature. To study hydrogen adsorption we have developed a new procedure named thermoadsorption (TA), where the sample is first exposed to a deuterium atom beam at high temperature and then, while being continuously exposed to the atom beam, the sample is gradually cooled down. In contrast to the usual temperature programmed desorption spectroscopy, where sites are being emptied during sample heating [2], we are in this case observing filling of different adsorption sites during the sample cooling. The main goal of this study is to obtain the temperature dependence of the deuterium surface areal density on polycrystalline tungsten, in the temperature range relevant for the future magnetically confined fusion device, ITER. The dynamics of hydrogen atom adsorption on tungsten are described by an extension of a kinetic model by Jackson et al. [25], which is described to some detail in Section 2. Beside TA, the isotope exchange was also studied on tungsten sample. This process is important due to its fundamental character, one pre-adsorbed isotope species being replaced by the other one and also due to its possible application in fusion for tritium removal from the tokamak wall. The isotope exchange was studied at 485 K sample temperature where different surface states were populated.

The diagnostic tool used in the present study is the ion beam method Elastic Recoil Detection Analysis (ERDA). The study was performed *in situ* and in real time. Although the ERDA method is providing the depth profile of the hydrogen concentration up to 400 nm in tungsten, the surface part of this profile is dominant since hydrogen diffusion from surface to bulk is small allowing clear study of surface processes. Moreover, ERDA is one of the rare techniques that can give simultaneously absolute hydrogen concentrations for both isotopes, H and D. Therefore it is an excellent method for observing the above described phenomena (especially isotope exchange), since both isotopes, H and D, are followed simultaneously.

2. Processes on the surface and kinetic model

In order to discuss the experimental results let us first describe the processes occurring on a surface being exposed to a constant flux of hydrogen (H or D) atoms. The atoms that approach the clean surface feel an attractive potential due to the interaction between its unpaired electron and electrons from the metal gaining about 2.9 eV of energy for tungsten [2,10] (around 2.4 eV on most of the metals [26,27]). This energy is equivalent to the binding energy of a single hydrogen atom on a metal surface E_{H-M}. Consequently, an incoming atom can be trapped on the surface with a certain probability. It can also recombine with a previously adsorbed atom, producing a hydrogen molecule which leaves the surface, the so-called Eley–Rideal (ER) recombination [27,28]. Generally, an atom cannot dissipate all the available energy immediately after being

trapped on the surface but some time is needed before it is thermalized. These atoms hop on the surface and during hopping they can recombine with an adsorbed atom, producing a molecule. This is the so-called hot-atom concept of the recombination mechanism [29]. Since we were observing the temperature dependence of the atom interaction with the surface which is becoming increasingly saturated, we additionally need to consider the Langmuir–Hinshelwood (LH) recombination process [28]. This is a thermally activated process, where two adsorbed atoms diffuse on the surface [30] and if they come close to each other, they can recombine and desorb as hydrogen molecule. Atom diffusion and desorption from the surface is appreciable only if the surface temperature is high enough, above 300 K for W [2].

In order to describe the phenomena observed on the surface, a model needs to be used which has to include all relevant processes. There are two kinetic models [25,31] that include the main processes occurring on the surface exposed to H atoms with pre-adsorbed D atoms and considering that the LH mechanism has negligible contribution due to low surface temperature ($T < 200$ K). We extend a model developed by Jackson et al. [25] by including the LH mechanism, since in our case the temperature is well above 300 K. We studied hydrogen interaction with the surface by exposing the surface to a flux of a particular hydrogen isotope, where the sample temperature was either constant or varied. In the case of the isotope exchange the sample had one isotope pre-adsorbed on the surface and then the surface was exposed to the other isotope at constant sample temperature.

We will describe the processes involved in isotopic exchange, which exhibits the maximum variety of process combinations. Let us consider the processes on the surface initially partially covered by adsorbed D, which is then exposed to a flux Φ_H of H atoms. The surface sites that are empty, H-occupied and D-occupied are denoted as S, H_S and D_S, while the hot atoms (HA) are denoted by H^* and D^*. The free atom in the surrounding gas is denoted as H and when producing hydrogen molecules they are considered to be desorbed from the surface. The same letters in parentheses [] denote the corresponding surface concentrations expressed in monolayers or areal densities expressed in atoms per cm^2. A monolayer (ML) denotes a full coverage of adsorbing species on the surface with atom density N, typically of the order 10^{15}–10^{16} cm^{-2}, depending on the surface atomic structure.

One has to consider the following processes:
Single encounter reactions:

(I) $H + D_S \rightarrow HD + S$ $\{\sigma_{HD}\}$ [ER recombination]
(II) $H + H_S \rightarrow H_2 + S$ $\{\sigma_{HH}\}$ [ER recombination]
(III) $H + S(H_S, D_S) \rightarrow H + S$ $\{P_r\}$ [Reflection]

Hot atom generation by incoming atom trapping:

(IV) $H + D_S \rightarrow H_S + D^*$ $\{\varepsilon_{HD}\}$
(V) $H + H_S \rightarrow H_S + H^*$ $\{\varepsilon_H\}$
(VI) $H + D_S \rightarrow H^* + D_S$ $\{\varepsilon_D\}$
(VII) $H + S \rightarrow H^* + S$ $\{\varepsilon_S\}$

HA-type reactions:

(VIII) $H^* + S \rightarrow H_S$ $\{s_H\}$ [Sticking]
(IX) $D^* + S \rightarrow D_S$ $\{s_D\}$ [Sticking]
(X) $H^* + H_S \rightarrow H_2$ $\{p_{HH}\}$ [HA recombination]
(XI) $H^* + D_S \rightarrow HD$ $\{p_{HD}\}$ [HA recombination]
(XII) $D^* + H_S \rightarrow HD$ $\{p_{DH}\}$ [HA recombination]
(XIII) $D^* + D_S \rightarrow D_2$ $\{p_{DD}\}$ [HA recombination]