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Probability of absorption/implantation of low-energy H_2^+ ions in O-covered vanadium

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Abstract

Energy dependence of the absorption/implantation probability, α_{ab}, of H_2^+ ions in vanadium covered by an oxygen monolayer was studied in the range 0.5–300 eV by plasma-membrane techniques. In contrast to what one would expect in the case of a clean surface, α_{ab} was found: (1) to be appreciably smaller than 1 ($\alpha_{ab} \approx 0.2$) at the lowest energies, and (2) to *monotonically* increase with ion energy, with a particularly steep rise in the range 0.5 to ~7 eV – just where α_{ab} is expected to sharply decrease at a clean surface.

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1. Introduction

Interactions of low-energy hydrogen particles with fusion materials ranks among the main issues of PSI in fusion devices. The subject is known to be rather difficult for investigations, in particular, because of an important role played by chemical composition of the surface at low energies [1–4]. Information on the reflection/trapping of eV energy particles is mainly obtained from calculations for neutral atoms, with the metal surface described by a uniform planar attractive potential (the 'binding energy') [1–4]. If such an approach may be acceptable for a clean surface, it is hardly satisfactory for a real surface covered by nonmetallic impurities which exhibits a marked heterogeneity [5,6].

The subject has been so far poorly investigated experimentally, for it is difficult to get an ion beam of an energy E_0 below hundreds of eV. Sophisticated methods such as glancing-incidence ion beam [7] or heteronuclear ions (e.g. ArD^+ [3,4]) have been employed to bypass the difficulty. However a substantial specificity of these interesting methods makes the data somewhat ambiguous. Hence attempts at obtaining eV particles directly from plasma were also undertaken [8].

An impurity monolayer (e.g. O on V [5] and Nb [6], C and S on Pd [6]) was found to reduce the absorption probability for *thermal* atoms from ~1 [9] to 0.2–0.3. How does behave the absorption

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probability $\alpha_{ab}(E_0)$ when *eV particles* bombard the surface covered by light impurity? Is there a deep minimum in $\alpha_{ab}(E_0)$ at a few eV with $\alpha_{ab} \approx 1$ at lower E_0, as that is predicted by the trapping probability calculations [1–4]?

V covered by a monolayer of O was used as a fusion-relevant material. We investigated the absorption/implantation probability of H_2^+ ions, $\alpha_{ab}(E_0)$, starting from $E_0 < 1$ eV. Such low energies became achievable only recently [10] due to the combination of plasma and membrane techniques, which also allows studying $\alpha_{ab}(E_0)$ in the steady-state regime at the fusion-relevant densities of ion flux ($>10^{16}$ ion/(cm^2 s)) and with an unlimited fluence. The first results obtained by this method are presented below.

2. Experimental techniques

We can control the incident ion energy with an accuracy $\sim kT_i$ by biasing the sample inserted in the hydrogen plasma (Fig. 1). If the sample is a membrane, the steady-state ion-driven permeation flux, j_{IDP}, can be presented as:

$$j_{IDP} = j_i / e\alpha_{ab}(E_0)\beta, \quad (1)$$

where j_i is the ion current density, e the electron charge, and β the probability that the absorbed ion permeates through the membrane. If β is known and is not changing with E_0, one can find $\alpha_{ab}(E_0)$ from j_{IDP}.

If vanadium is staying in vacuum at an elevated temperature, its surface is covered by O monolayer equilibrated with the solute oxygen [5]. Such a coverage brings about the ion-driven superpermeation with $\beta \approx 0.5$ [6,10,11]. The complication is that β may be changing with E_0 because of the chemical and physical sputtering of O [11]. Fortunately, the O coverage, and hence β, were found [10] to remain quite stable under ion bombardment, if the temperature is high enough and if solute O concentration is sufficient. To meet these conditions, we operated with our resistively heated tubular V membrane (1 cm diameter, 10 cm length, and 0.01 cm wall thickness) at 690 °C and doped it with 2.9 at.% of O.

The membrane sample is placed in the center of a chamber filled by uniform hydrogen plasma generated by the electric discharge between a set of Ta cathodes located close to the chamber walls in a multi-cusp magnetic field and the chamber side wall (Fig. 1) [11,12]. Generated in the discharge are H^+, H_2^+ and H_3^+ ions, but H^+ concentration is usually much smaller than that of H_2^+/H_3^+ [11–13]; H_3^+ concentration may be significant, but only at pressures substantially higher than 0.4 Pa used in these experiments [12,13], so H_2^+ is the main ion component.

The UHV water-cooled plasma-membrane apparatus with a basic pressure $\sim 10^{-8}$ Pa had two turbomolecular pumps continuously pumped the up- and down-stream chambers.

The permeation flux was determined by hydrogen pressure increase in the down-stream chamber (Fig. 1) evacuated with a known pumping speed [6,11]. Switching on of the discharge at a *positive* (relative to the plasma) membrane bias produces a permeation flux due mainly to atomic hydrogen (Fig. 2) [10,11]. A *negative* biasing unblocks the ion flux to allow the ions to contribute to permeation (Fig. 2). With successive step-wise negative bias changes within one experimental run (Fig. 2), we can directly watch and compare the effects of

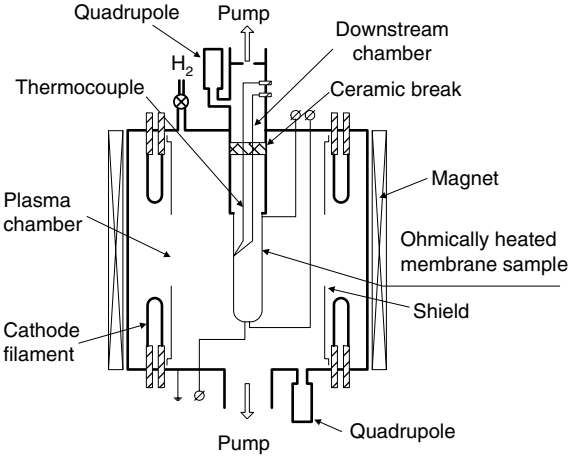

Fig. 1. Plasma-membrane setup.

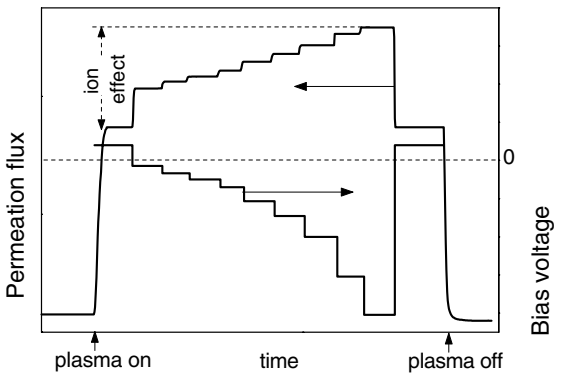

Fig. 2. The scheme of the experimental procedure.

different biases. Note that the system response to a bias change is as short as 6–7 s.

3. Experimental results

The dependence of ion-driven permeation flux, j_{IDP}, on the potential of membrane bias relative to the plasma, U_b, is presented in Fig. 3. Also presented is bias current, I_b, onto the membrane assembly. Technically, the sample is biased against ground (the chamber wall). U_b was found to be 1.4 V lower than this directly measured bias due to a positive plasma potential.

First, *the incident ion flux* can be determined from I_b. Bias current is $I_b = I_e + I_i$, where I_e and I_i are the electron and ion currents, respectively. When the negative bias is large enough ($U_b < -5$ V), I_b is almost completely determined by the ion current which remains almost constant in this voltage range (Fig. 3). Still the positive I_b branch starts declining at a *negative* potential ($U_b > -5$ V) to come down to 0 at the floating potential ($U_b \approx -2$ eV). That occurs due to a significant I_e contribution into I_b even at $U_b < 0$. However, there are no physical reasons for changes in the I_i behavior, as long as $U_b < 0$. Thus we extrapolated the ion current from the range of a more negative bias onto -5 V $< U_b < 0$ (solid line in Fig. 3).

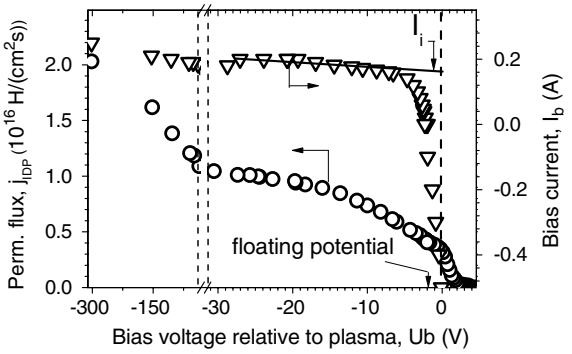

Fig. 3. Ion-driven permeation flux and current to the membrane assembly vs membrane bias. A bend of j_{IDP} at $U_b = 0$ indicates that incident ion flux stops to change at $U_b < 0$ and the ion energy becomes only factor determining j_{IDP}.

Next, one can find *ion temperature*, T_i, as follows. When the bias comes from negative to positive, the incident ion flux starts getting cutoff to cause a much steeper j_{IDP} decline (Fig. 3). At $U_b \approx +2$ V, j_{IDP} approaches 0, meaning that the ion cut off occurs within the range $0 < U_b < 2$ V. That yields $T_i \approx 0.7$ eV (the typical value for such a plasma [11,12]).

Energy dependencies of the ion absorption probability, $\alpha_{ab}(E_0)$, presented in Fig. 4 was obtained from the experimental data (Fig. 3) by Eq. (1) on assuming that (i) the incident ion flux consists of only H_2^+, and (ii) $\beta = 0.5$ at any E_0 (Section 2). With these assumptions, the absorption probability as presented in Fig. 4 was calculated like: $\alpha_{ab} = j_{IDP} \cdot e/j_i$, with j_{IDP} counted in H atoms per unit area. The H_2^+ ion translational energy, E_0, was taken $-U_b$ (at $U_b < 0$), which makes $E_0 = -0.5 \cdot U_b$ per nucleon, as plotted in Fig. 4. The errors indicated in Fig. 4(b) are obtained with taking $\pm kT_i = \pm 0.35$ eV/nucleon for E_0 determination accuracy (proceeding from H_2^+ ion temperature $T_i \approx 0.7$ eV).

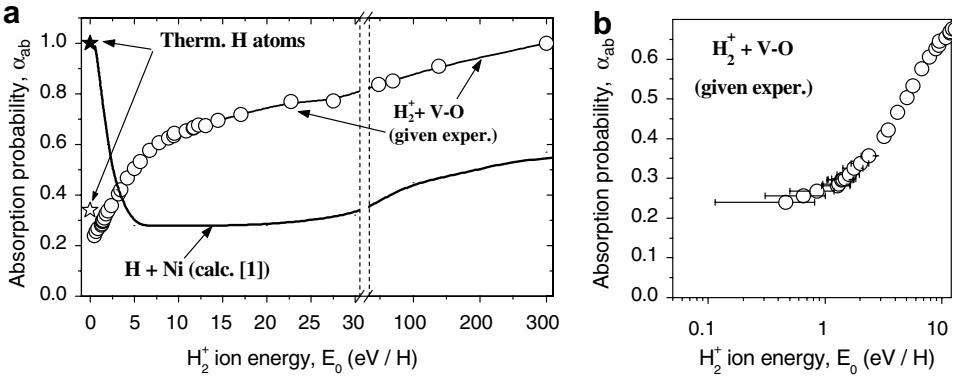

Fig. 4. Energy dependence of absorption probability. (a) Our experimental data for polycrystalline Vanadium *covered by monolayer of* O and H_2^+ ions are compared with calculations for a *clean* metal surface (Ni) and H atoms [1]. Experimental data for *thermal atoms* are also presented: solid star is for *clean* surface of transition metals [9], open star for V(1 0 0) *covered by a monolayer of* O [5]. (b) Our data at lowest energies.

At higher energies ($E_0 > \sim 10$ eV/nucleon), our data on α_{ab} immediately yield *the reflection probability*: $R_N = 1 -$ implantation probability $= 1 - \alpha_{ab}$. However, *eV particles* rather stick to the surface than are implanted. Such trapped atoms can be thermalized and released back without being absorbed, i.e.: $R_N = 1 -$ trapping probability $\leqslant 1 - \alpha_{ab}$. Hence one only can find the upper R_N limit from α_{ab} at eV energies.

4. Discussion

First, one should note that the actual incident particle energy may be higher than the initial ion energy E_0 presented in Fig. 4 because the ions approaching a metal surface gain an extra energy due to the *image forces*. This energy is the higher, the smaller the distance from the surface, r, at which the neutralization occurs. If r is 1–1.5 Å, as that was found for a clean surface in Ref. [7], the gain amounts to 1–2 eV/nucleon.

4.1. Possible transformations of the H_2^+ ions

H_2^+ ions get neutralized at approaching the surface, and if $E_0 > 2.2$ eV/H (the H_2 molecule bonding energy), the collision can be considered as interactions of two separate atoms with the surface. If $E_0 < 2.2$ eV/H, the majority of H_2^+ ions still can be transformed into atoms through H_2 molecule dissociation from an antibonding state obtained in H_2^+ neutralization [7]. Thus it is relevant to compare our results on H_2^+ ions with the behavior of H atoms (Fig. 4(a)). However, the excited H_2 molecules may release their excess of energy obtained at neutralization [14]; in such a case, incident on the surface will be energetic H_2 molecules (with $E_0 < 2.2$ eV/H).

4.2. The monotonous $\alpha(E_0)$ behavior

α_{ab} *monotonically* grows with E_0, in contrast to predictions of the calculations of H atom trapping/reflection at a uniform attractive potential, E_s, ascribed to the clean surface [2]: like the non-monotonous $\alpha_{ab}(E_0)$ dependence calculated for Ni with $E_s = 3$ eV as presented in Fig. 4(a) (targets of Ni and V are very much alike due to the close masses and nuclear charges).

One can predict with no special calculations a non-monotonous behavior of $\alpha_{ab}(E_0)$ at H atom interactions with a *clean* metal surface. True, the experimentally measured α_{ab} gradually decreases with decreasing energy from $\alpha_{ab} \approx 1$ in the keV range to 0.2–0.3 at $E_0 \approx 100$ eV [1], but α_{ab} becomes $\sim$1 again for the thermal H atoms [9]. Thus $\alpha_{ab}(E_0)$ inevitably is to pass through a deep minimum somewhere at E_0 comparable to E_s.

One can reckon by similar reasoning that such a non-monotonous $\alpha_{ab}(E_0)$ behavior should not necessarily occur, and is even improbable, at interactions of hydrogen ions (atomic or molecular) with metal surface *covered by light impurity*: α_{ab} for keV particles is close to 1 for such a surface too, whereas α_{ab} for the thermal H atoms is known to be 0.2–0.3, unlike 1 for a clean surface (Fig. 4(a)) [5,6]. Therefore, if H_2^+ ions reach the surface as separate atoms, $\alpha_{ab}(E_0)$ may pass through a shallow minimum, but even that only in the case, when α_{ab} is getting smaller than 0.2–0.3 somewhere in the range of tens of eV. Still that is rather unlikely because the light impurities reduce hydrogen ion reflection. Proceeding from similar arguments one can conclude that a minimum in $\alpha_{ab}(E_0)$ is even less probable, if H_2^+ ions get transformed into energetic H_2 molecules.

In contrast to our arguments and experimental results, the authors of Ref. [3] found a non-monotonous dependence $\alpha_{ab}(E_0)$ for the trapping of deuterium by O-covered Nb acted upon by D_3^+ and ArD^+: similarly to the H–Ni curve in Fig. 4(a). This divergence may be due to a great difference in the fluences and sample temperatures: 10^{14}–10^{15} D/cm^2 and presumably, $\sim$20 °C in the Ref. [3] – against 10^{19}–10^{20} H/cm^2 (in the steady-state regime) and 690 °C in our experiment. The former results, obtained at the low fluence and temperature, may refer to the surface trapping rather than to absorption in the bulk.

4.3. Drastic change of $\alpha(E_0)$ at eV energies

A sharp α_{ab} *increase* with E_0 occurs in the narrow energy range: $0.5 < E_0 < \sim 7$ eV/nucleon (Fig. 4(a)). That might be explained in the two ways:

(A) The impurity coverage makes α_{ab} substantially smaller than 1 at the lowest energies (e.g. for thermal atoms). That may occur because the H atom binding energy is small enough at most of the surface area (70–80%) for the incoming atoms to be instantly desorbed (like He). The only way how atoms can be absorbed into the bulk through the *whole* surface is their *implantation* into a depth of at least one layer. The probability of that approaches 1 at $E_0 = 5$–10 eV.

(B) Another explanation may be grounded on the specific ability of molecular ions (H_2^+) to transfer their neutralization energy, E_n, to an extra translational energy, ΔE, of H atoms flying away from one the other at the breakup of an H_2 molecule excited into an antibonding state at H_2^+ neutralization. Resulting from the atomic motion with respect to the molecular center-of-mass, the energy component normal to the surface will change from its initial value E_0 to:

$$E_{1_\perp} = \left(\sqrt{E_0} \pm \sqrt{\Delta E}\cos\vartheta\right)^2, \quad (2)$$

where ϑ is the angle between molecule axis and normal to the surface. A half of the atoms will gain an additional momentum directed *from* the surface (minus in Eq. (2)), and if $\Delta E \cdot \cos\vartheta > E_0$, they will never reach the surface. In general, there is a range of possible ΔE limited from the above by a certain ΔE_{max}. If ΔE obtained by most of the atoms is substantially greater than the lowest ion energy E_0 in our experiment, nearly a half of the atoms will not reach the surface at the lowest E_0. But the incident flux will grow with E_0 to be finally doubled when E_0 exceeds ΔE_{max}. ΔE_{max} must not be greater than $E_n/2 = (I_i - \varphi)/2$ eV/nucleon, where I_i is the H_2 ionization potential, and φ is the work function for V. With $I_i = 15.4$ eV and $\varphi = 4.1$ eV, one gets $\Delta E_{max} \leqslant 6$ eV/atom.

Thus the flux actually reaching the surface can depend on E_0 at a constant incident H_2^+ ion flux, ultimately doubling with E_0 growth and causing $\alpha_{ab}(E_0)$ to grow very sharply within a narrow E_0 range: $E_{0min} < E_0 < \Delta E_{max}$. In fact, the experimentally obtained α_{ab} does exhibit a *more than 2-fold increase* within $0.5 < E_0 < \sim 7$ eV/nucleon range (Fig. 4(a)), with $\alpha_{ab}(E_0)$ dependence becoming substantially weaker at higher E_0.

5. Conclusions

Energy dependence of the absorption/implantation probability, α_{ab}, of H_2^+ ions in vanadium covered by an oxygen monolayer was studied in the range 0.5–300 eV in the steady-state regime at the fusion-relevant densities of ion flux ($>10^{16}$ ion/(cm^2 s)) and with an unlimited fluence. In contrast to what one would expect in the case of a clean surface, α_{ab} was found: (1) to be appreciably smaller than 1 ($\alpha_{ab} \approx 0.2$) at the lowest energies, and (2) to *monotonically* increase with ion energy, with a particularly steep rise in the range 0.5 to $\sim$7 eV – just where α_{ab} is expected to sharply decrease at a clean surface.

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