Anomalous isotope effect in the permeation, retention, and reemission at interaction of energetic hydrogen with niobium

A.I. Livshits[1], M.E. Notkin[1], and M. Bacal[2]

[1] Bonch-Bruyevich University of Telecommunications, 61 Moika, St Petersburg 191186, Russia

[2] Laboratoire de Physique et de Technologie des Plasmas, U.M.R. 7648 du C.N.R.S., École Polytechnique, 91128 Palaiseau, France

Abstract

A niobium membrane sample was placed in H or D plasma and electrically biased. Isotope effects for H vs. D in factors of 20, $\sqrt{40}$ and 40, respectively, were observed in plasma driven permeation, retention, and in the reemission, within a narrow range of bias voltages (40–80 V) at the lowest metal temperature investigated (910 K). The phenomenon occurred at the "superpermeation" of suprathermal hydrogen arising from an oxygen monolayer at the metal surface. The phenomenon is supposed to be caused by dynamics of the oxygen monolayer under the action of ion sputtering and surface segregation of dissolved O. Such and even much stronger isotope effects are also expected on other metals with a similar "real" surface. This isotope effect may be important for D/T-mixture recycling, retention and permeation at its interactions with plasma facing components of fusion reactors as well as for the applications of superpermeable membranes for pumping of hydrogen isotopes and their separation from He.

1. INTRODUCTION

Studies involving the simplest atomic particles such as hydrogen molecules, atoms, and ions, present a particular significance for the physics of interactions of atomic particles with solids. Isotope effects in hydrogen/solid systems is a typical subject of investigations, as the effect of particle mass on phenomena observed is an important feature of theoretical speculations [1,2]. Of great interest is, e.g., the strong isotope effect in the diffusivity of H, D, and T in V, Nb and Ta at temperatures $< -50°$ C [2,3].

Peculiar isotope effects in hydrogen/solid systems become particularly important in view of the development of fusion reactors where energetic D/T particles will interact with plasma facing components.

This includes such phenomena as hydrogen retention, permeation and reemission responsible for D/T recycling and tritium safety. *Effects of surface chemistry* play a very special role in these phenomena, if hydrogen particles posses a *suprathermal* energy [4]. A monolayer of nonmetallic impurity that usually covers a metal "real" surface for e.g. may drastically impede reemission, and at the same time radically enhance retention and permeation. Moreover, permeation even may reach up to the "superpermeation" due to such a film, meaning that a metal membrane of macroscopic thickness becomes virtually "transparent" to hydrogen particles whose energy exceeds ~ 1eV. The suppressed reemission of D/T particles as well as their enhanced retention and permeation at the interaction with plasma facing materials are extremely undesirable during normal reactor operation as well as for safety reasons. On the other hand, the superpermeation and enhanced absorption may be an effective means of D/T pumping [5] and separation from He [6] in fusion reactors and their models.

A superpermeable Nb membrane is used as a sample in this study. The paper is focused on the more than an order–of–magnitude difference in Nb permeability to hydrogen and deuterium at bombarding the metal by H and D ions within a narrow range of ion energies (tens of eV) in a definite range of metal temperatures (~ 900 K). If the authors' interpretation is correct, then, (1) the effect may be a few orders of magnitude greater, (2) a similar isotope effect is to be expected on other metals as well, and, (3) a similar effect does appear in hydrogen absorption and reemission.

2. EXPERIMENTAL SETUP

The present investigation was carried out at the plasma – membrane setup described in more details in Refs. [7]. A resistively heated tubular membrane of Nb

(1 cm in diameter, 18 cm long and 0.01 cm wall thickness) is immersed into a hydrogen or deuterium plasma filling a chamber 44 cm in diameter in height and 45 cm as shown in Fig. 1 (in fact *two* of the same membrane samples are installed simultaneously). The plasma is generated by an electric discharge between a set of sixteen hot tantalum cathode filaments located close to the chamber wall in a multicusp magnetic field and the chamber wall, serving as the anode [8]. The plasma density is about 5×10^{10} cm^{-3}, and the electron temperature is approximately 0.6 eV [8] during the typical conditions of this experiment (discharge current $25 - 30$ A, discharge voltage of 60-70 V, gas pressure 2 to 4 mTorr). H_2^+, H_3^+ and D_2^+, D_3^+ are the main ion species in hydrogen and deuterium plasmas, respectively. The ion temperature is in a few tenths of eV. The membrane sample is electrically insulated, and the incident ion energy may be varied up to 250 eV with biasing the membrane relative to plasma (practically, relative to the wall-anode whose potential is close to that of plasma). The ion current density is ~ 3 mA/cm^2, nearly the same over the whole range of negative bias voltages investigated.

Two turbo-molecular pumps (50 l/s each) continuously operate in the down– and upstream chambers. The total pressure of impurities in the input chamber was in the order of 10^{-6} Torr during plasma operation, and a quadrupole mass spectrometer indicated that CO was the main impurity, and H_2O the next one (2×10^{-7} Torr). The pressure in the up- and downstream chambers is measured with Bayard-Alpert, Pirani and Baracell gauges.

The membrane specimen is made of a polycrystalline Nb foil. Auger Electron Spectroscopy (AES) analysis of the membrane material showed that oxygen and carbon were the main nonmetallic impurities that remained, in the form of a monolayer coating, on the surface of specimen after heating ($> 550°C$) in vacuum. The same impurities segregated again to the surface from the metal bulk after the surface was submitted to Ar$^+$ ion bombardment followed with heating in UHV. The membrane sample was subjected to a 1500 K heating in vacuum prior to the experiment.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Experimental results. Dependencies on bias/energy of the steady-state permeation fluxes driven by H and D plasmas, j_H and j_D, respectively, and of the isotope effect, j_H / j_D, are presented in Fig. 2. One can single out three
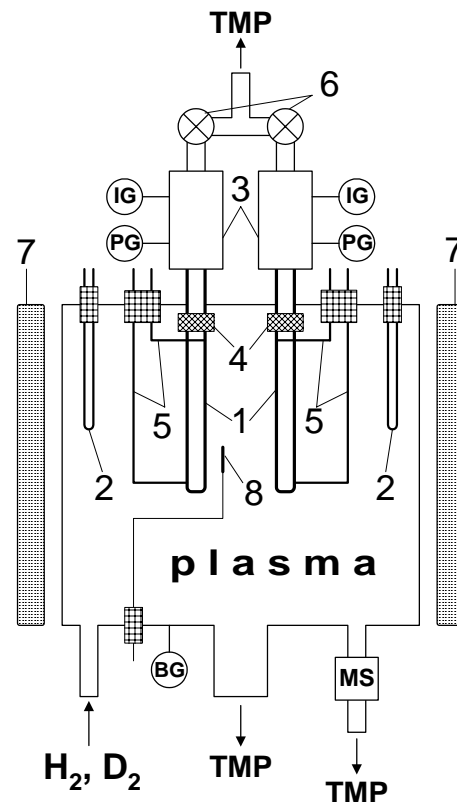

FIG. 1. Schematic of the plasma-membrane setup. 1 - membranes, 2 - filaments, 3 - downstream vacuum chambers, 4 - insulators, 5 - heavy-current leads, 6 - valves, 7 - multicusp magnet system, 8 - electrostatic probe; IG - ionization gauge, PG - Pirani gauge, BG - Baracell gauge, MS - quadrupole mass spectrometer, TMP - turbomolecular pump.

different zones: (1) at a low incident energy, the permeation is energy/bias-independent in the first approximation; (2) with energy rising, the permeation is dropping; and, (3) at a further energy increase, the permeation becomes almost energy-independent again, but at a lower level. At the lowest temperature, all the three zones are most pronounced, whereas at the highest temperature, the high-permeation zone is spreading over the entire energy range investigated. Note that ion species bombarding the sample were mainly H_2^+ / D_2^+ and H_3^+ / D_3^+. The energy per nucleon for these ions is smaller by a factor 2 and 3, respectively, than the incident ion energy indicated.

The isotope effect is quite ordinary everywhere except for a narrow range of incident energies at the lowest studied temperature (910 K) where j_H/j_D exhibits a sharp maximum with a height ~20. The anomaly is due to a sharp decrease in D permeation between 30 and

60 eV, while H permeation still remaining at its highest value (Fig. 2c).

The role of nonmetallic monolayer. As indicated above, the Auger Electron Spectroscopy Analysis [7, 9] shows the presence of a very stable O monolayer on Nb surface remaining after the dissolution in metal bulk of virgin polyatomic oxide film during heating in high vacuum at $T > 900$ K. Such a monolayer gives rise to potential barriers, E_u and E_d, at the membrane up– and downstream sides that drastically hinder the dissociation of H_2/D_2 molecules at their thermal absorption in the metal, with the probabilities of these processes (sticking coefficients), α_u and α_d, being [4]:

$$\alpha_u = B_u \exp\left(-\frac{E_u}{kT}\right) ; \quad \alpha_d = B_d \exp\left(-\frac{E_d}{kT}\right), \quad (1)$$

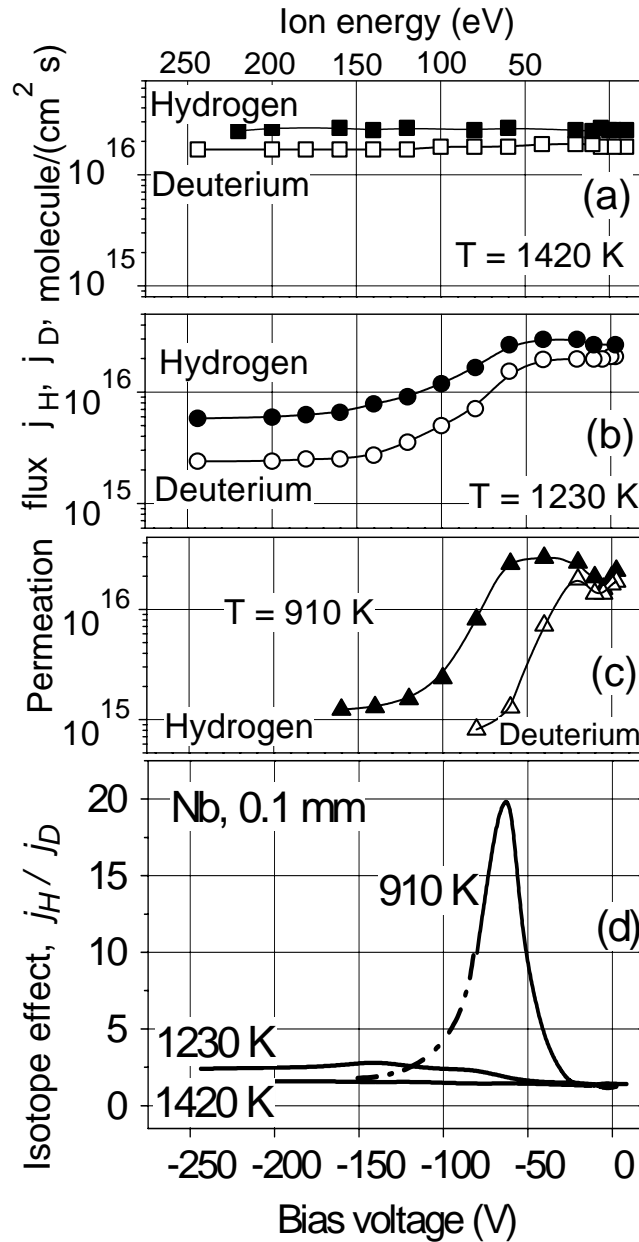where B_u and B_d are coefficients that are temperature independent in the first approximation. The barriers

FIG. 2. Dependence of the plasma driven permeation fluxes j_H and j_D (a, b and c) and of the isotopic effect in permeation j_H/j_D (d) on bias voltage (bombarding ion energy) at three membrane temperatures. The ion current density is ~3 mA/cm^2 (mainly H_2^+, H_3^+ and D_2^+, D_3^+ [7]). The incident flux of H/D atoms of near-thermal energy is ~ 10^{17} cm^{-2}s^{-1} [7].

prevent the association of absorbed H/D atoms into H$_2$/D$_2$ molecules at their thermal evolution as well [4,7], with the desorption rate constants k_{ru} and k_{rd} related to α_u and α_d as:

$$k_{ru} = \frac{z}{S^2} \times \alpha_u, \quad k_{rd} = \frac{z}{S^2} \times \alpha_d, \qquad (2)$$

where S is a solubility constant of H$_2$/D$_2$ in metal, and z is the kinetic gas theory coefficient.

Hydrogen evolution may be inhibited with such barriers to such an extent that the absorbed atoms reach the opposite side of the membrane with a greater probability than are reemitted back. The downstream barrier also reflects the absorbed atoms to make them "oscillate" between the two boundaries by way of usual random-walk diffusion. As a result, the absorbed atoms "forget" their starting position, with their desorption through the up– or downstream surfaces depending only on relative values of the desorption rate constants k_{ru} and k_{rd}. Hence the steady state permeation flux, j, is given by:

$$j \approx j_{inc}\xi \times \frac{1}{1 + k_{ru}/k_{rd}} = j_{inc}\xi \times \frac{1}{1 + \alpha_u/\alpha_d}, \quad (3)$$

where j_{inc} is an incident flux, and ξ is a probability of absorption at one impact on the surface. In the specific case of the Group Va metals (including Nb), such a permeation regime (the so called regime of "strong internal reflection" [10], or "RR-regime" [11]) occurs over practically the whole range of temperatures, flux densities, and membrane thickness of interest [4, 7].

Suprathermal hydrogen particles whose energy (kinetic, internal, or chemical) exceeds ~ 1 eV may pass *freely* into metal in spite of the barrier, i.e., ξ is *independent of T* and varies between ~ 0.1 and 1, conditioned only by reflection coefficient [12]. Accordingly, *the permeation of suprathermal particles* is given by:

$$j \approx j_{inc} \times \frac{0.1 - 1}{1 + \alpha_u/\alpha_d}$$
$$\xrightarrow{\alpha_u \leq \alpha_d} \quad j_{inc} \times (0.1 - 1). \qquad (4)$$

Thus, due to the barrier generated by a nonmetallic film, the permeation flux may become comparable to the incident one and temperature-independent. That is the mentioned above "superpermeation" (e.g., Refs. [4,7]). The superpermeation of both the H and D atoms of thermal kinetic energies and of more energetic particles was

demonstrated on many metals (including Nb) with controlled chemical composition of the surfaces (e.g., Refs. [4, 13]). The plasma driven permeation presented in Fig. 2 also is *superpermeation over the low bias/energy range* (here, $\alpha_u \approx \alpha_d$), which is proven, e.g., by temperature independence of j_H and j_D (Fig. 2a-c); that conforms with previous results obtained on the same apparatus with H plasma [7].

The role of sputtering. The drop in permeation at higher energies (Fig. 2b,c) implies an increase of reemission. The direct ion-induced reemission is negligible at these rather high T [4, 13], but ion bombardment may strongly enhance the *thermal* absorption/desorption processes due to sputtering of the O monolayer [4,7] at ion energies exceeding the *sputtering threshold* (just for instance, the difference in α and in k_r for the clean surface of a transition metal and for the surface covered by nonmetallic monolayer is typically in excess of 3 orders of magnitude [4, 14]). We denote with upper indices H^+ and D^+ the kinetic coefficients of the *thermal* boundary processes occurring under ion bombardment: $\alpha_u^{H^+}, \alpha_u^{D^+}, k_{ru}^{H^+}, k_{ru}^{D^+}$ (the kinetic coefficients ξ and α_d as well as the incident flux j_{inc} in the above equations also may depend on hydrogen isotope mass. However, such a difference only may amount to the usual isotope effect factor of $\sqrt{2}$, which is not the point of this our treatment). Then $\alpha_u^{H^+, D^+}$ is a function of incident ion energy E, with the permeation flux $j_{H,D}$ (i.e., j_H or j_D) and the isotope effect, j_H/j_D given by:

$$j_{H,D} = (0.1 - 1)j_{inc} \times \frac{1}{1 + \alpha_u^{H^+, D^+}(E)/\alpha_d}; \quad (5)$$

$$\frac{j_H}{j_D} = \frac{1 + \alpha_u^{D^+}(E)/\alpha_d}{1 + \alpha_u^{H^+}(E)/\alpha_d}. \qquad (6)$$

Thus the idea is that the steep permeation drop and the anomalous isotope effect observed when the incident energy exceeds a certain value (Fig. 2) are due to the energy exceeding the threshold of O monolayer sputtering and to a drastic change in the rate of sputtering in the vicinity of threshold energy, which makes $\alpha_u^{H^+}, \alpha_u^{D^+}$ in eqs. (5) and (6) change dramatically.

To illustrate the near threshold behavior of the coefficient of sputtering by H$^+$ and D$^+$ ions, Y_{H^+, D^+}, we used an empirical equation by Bohdansky et al. [15] for sputtering of metals and their compounds by low-energy

light ions:

$$Y_{H^+,D^+} = 0.0064 \cdot M_O \gamma_{H,D}^{\frac{5}{3}} \times \left(\frac{E}{E_{th}^{H^+,D^+}} \right)^{\frac{1}{4}} \times \left(1 - \frac{E_{th}^{H^+,D^+}}{E} \right)^{\frac{7}{2}}$$

(7)

here M_O is the mass of O atom in a.m.u., $\gamma_{H,D}$ is the reduced mass: $\gamma_{H,D} = 4M_{H,D} \cdot M_O/(M_{H,D}+M_O)^2$, $E_{th}^{H^+,D^+}$ is the threshold energy of sputtering: $E_{th}^{H^+,D^+} = \dfrac{U_{Nb-O}}{\gamma_{H,D}\left(1-\gamma_{H,D}\right)}$, and U_{Nb-O} is bonding energy of an O atom. We applied eq. (7) to the sputtering of surface O atoms from NbO, so we took for the bonding energy that in NbO: $U_{Nb-O} = 6.95$ eV [16]. The result is presented in Fig. 3. Though this calculation hardly describes the sputtering of *chemisorbed* O atoms (our case) quantitatively, Fig. 3 does demonstrate the main trends: a dramatic change in Y_{H^+,D^+} with E changing, and a drastic isotope effect in the near threshold energy range.

The simplest case would be, if one might disregard a possible continuous repair of sputtered nonmetallic monolayer even in the near-threshold energy range where the sputtering coefficient is relatively small (Fig. 3). In such a case, a smallest overstepping of $E_{th}^{H^+,D^+}$ would lead to a complete removal of nonmetallic monolayer from the upstream surface and, consequently, to an immense $\alpha_u^{H^+,D^+}$ rise. Thus, according to eq. (5) and as shown in Fig. 4, an orders-of-magnitude stepwise dropping of j_H and j_D should have been observed at $E \approx E_{th}^{H^+}$ and $E \approx E_{th}^{D^+}$, respectively, with *an orders-of-magnitude isotope effect* manifesting itself at
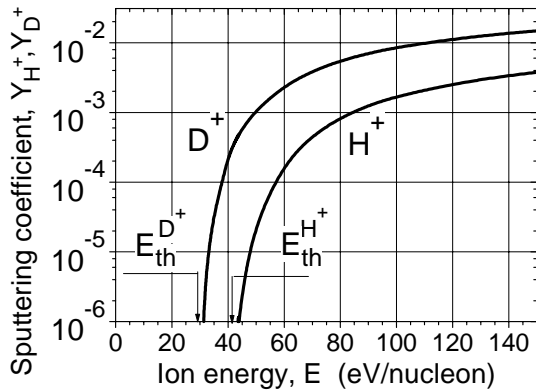
FIG. 3. Energy dependence of the sputtering coefficient of surface O atoms from NbO by H$^+$ and D$^+$ ions at perpendicular incidence calculated by empirical eq. (7).

$E_{th}^{D^+} < E < E_{th}^{H^+}$: the D$^+$ bombardment would have already brought about an orders-of-magnitude $\alpha_u^{D^+}$ rise up to $\alpha_u^{D^+} \approx 0.1$ (clean surface), while H$^+$ bombardment would not have yet changed $\alpha_u^{H^+}$ from its undisturbed value: $\alpha_u^{H^+} \approx \alpha_d$. Hence one would get $\dfrac{j_H}{j_D} \approx \dfrac{0.1}{2\alpha_d}$ at $E_{th}^{D^+} < E < E_{th}^{H^+}$ (eq. (6) and Fig. 4). Such an isotope effect, though decreasing at higher T (Fig. 4) due to α_d rising, still would remain very strong, as $\alpha_d \ll 0.1$ even at high T.

Effects of the dynamics of impurities. However, such a picture is at a variance with the reality (Fig. 2). A more realistic description must account for that oxygen monolayer may be dynamically restored during sputtering.

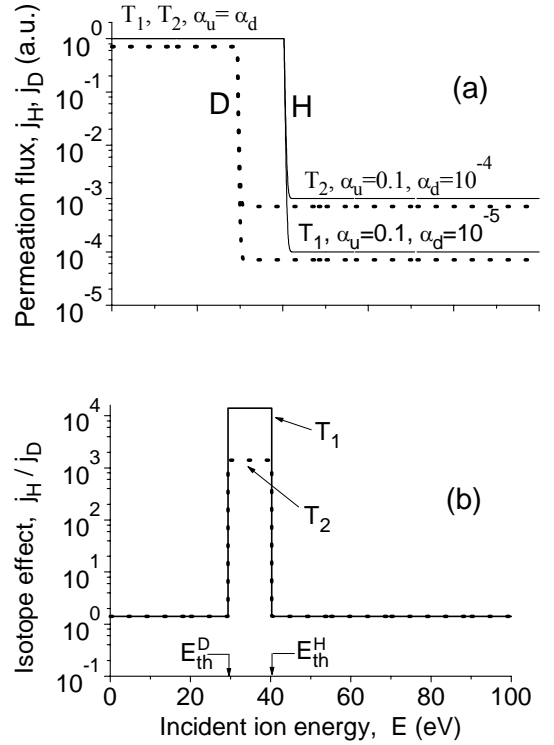*In the absence of sputtering*, O at the surface is

FIG. 4. Energy dependence of the permeation flux (a) and of the isotopic effect in permeation (b) calculated by eqs. (5) and (6) at two temperatures ($T_1 < T_2$) for the case when the rate of replenishment of the nonmetallic monolayer is negligible compared to the rate of its sputtering in near-threshold range. Taken as typical exemplifying values of α_d for an undisturbed downstream surface and of α_u for a clean upstream surface are: $\alpha_d(T_1) = 10^{-5}$, $\alpha_d(T_2) = 10^{-4}$ and $\alpha_u = 0.1$.

in a dynamic equilibrium with the O dissolved in the metallic lattice [17]:

$$\frac{\Theta_{Os}^{eq}}{1-\Theta_{Os}^{eq}} = A \cdot \exp\frac{G_{Nb}^{O}}{kT} \times \Theta_{Ov} \; ; \qquad (8)$$

here Θ_{Os}^{eq} is an equilibrium surface coverage with O, Θ_{Ov} an atomic ratio of O in the lattice, and G_{Nb}^{O} the heat of surface segregation of O ($G_{Nb}^{O} > 0$). Usually, a monolayer O coverage ($\Theta_{Os}^{eq} \approx 1$) exists even at $\Theta_{Ov} \ll 1$ [4,7,17,18] due to surface segregation. However, according to eq. (8), a definite equilibrium concentration of O-free sites, $\Theta_{f}^{eq} \equiv 1 - \Theta_{Os}^{eq}$, does always exist, with the number of such sites increasing with T.

The surface segregation [18] continues to maintain an O coverage even *under sputtering*. Hence sputtering never resulted in a complete cleaning of the upstream surface in our experiment – it damaged, but only slightly, the equilibrium monolayer ($\Theta_{O}^{eq} \approx 1$ was kept valid) [7,18] to maintain a certain steady-state concentration of O-free sites, $\Delta\Theta_{f}^{H^+,D^+}$ and in addition, their equilibrium concentration, Θ_{f}^{eq}. The O-free sites are centers of a facilitated thermal hydrogen absorption-desorption. Therefore, if $\Delta\Theta_{f}^{H^+,D^+} \geq \Theta_{f}^{eq}$, the ion bombardment may lead to a significant $\alpha_{u}^{H^+,D^+}$ increase, and, according to eq. (5), to a decreased permeation of suprathermal H/D particles. On accounting for that $\Delta\Theta_{f}^{H^+,D^+}$ depends on E, $M_{H,D}$, T, ion flux density, i_{H^+,D^+}, and on O diffusivity in Nb, D_O, and with using eq. (8), we formulate the condition of the strong effect of ion bombardment:

$$\Delta\Theta_{f}^{H^+,D^+}\left(i_{H^+,D^+}, E, M_{H,D}, D_O, T\right) \geq \frac{1}{A} \cdot \exp\left(-\frac{G_{Nb}^{O}}{kT}\right) \times \frac{1}{\Theta_{Ov}} \; .$$
$$(9)$$

The higher T, the harder to satisfy condition (9); that is so not only due to an exponential rise of the right-hand part with T, but also because of a decrease of the left part due to a faster filling of over-equilibrium O-free sites with migrating O atoms. Hence, the higher T, the farther superpermeation is spreading into the region of higher E (cf. Fig. 2a,b,c).

The same background seems to determine the disappearance of the anomalous isotope effect at higher T (Fig. 2d). The crucial point for the effect to take place consists in that the steady-state concentration of O-free sites is to be effectively augmented (eq. (9)) by ion

sputtering in an energy range *near the sputtering threshold*. However sputtering coefficients are rather small here (Fig. 3), and that is why the condition (9) could have been met in the *near-threshold energy range* only at the lowest temperature in our experiment (910 K), and at this T only the anomalous isotope effect was observed. Though fairly well pronounced, this isotope effect is still substantially smaller than that for the idealized case of a practically immobile O, as exemplified by Fig. 4. However, a permeation experiment with Nb may be staged at a substantially lower T, e.g., at ~ 600 [13] rather than 900 K. In such a case, O transport between the surface and lattice will be almost frozen, and one can approach much closer the hypothetical case of Fig. 4 with its *orders-of-magnitude isotope effect*.

The isotope effect in retention and reemission. As it follows from all the above, the primary underlying cause of the anomalous isotope effect in permeation is a large difference in the kinetic coefficients of thermal boundary processes, $\alpha_{u}^{H^+}$, $\alpha_{u}^{D^+}$, and $k_{ru}^{H^+}$, $k_{ru}^{D^+}$, at $E_{th}^{D} < E < E_{th}^{H}$. The isotope effect in the desorption/reemission rate constants, $k_{ru}^{H^+}$, $k_{ru}^{D^+}$ and $k_{ru}^{T^+}$, seems to be particularly important, since these constants are responsible for H/D/T reemission/recycling and retention in plasma facing materials in fusion devices. From eqs. (2) and (5), $k_{ru}^{D^+} / k_{ru}^{H^+} \approx 2 \cdot j_H / j_D$ at $j_H / j_D \gg 1$ (on assuming $\alpha_u \approx \alpha_d$ without sputtering). Thus *the isotope effect in the rate constant of H_2/D_2 desorption goes as high as 40* in our experiment at 910 K (Fig. 2). The steady-state concentration, c, during the interaction with an energetic hydrogen obeys the relations $c_{H,D,T} \propto 1/\sqrt{k_{ru}^{H^+,D^+,T^+}}$ [4]. Correspondingly, the isotope effect in retention, c_H/c_D, reaches $\sqrt{40}$.

The anomalous isotope effect in the absorption/desorption kinetics is by no means related to particular properties of the O-covered Nb: that must be a universal phenomenon to appear on all transition metals with a "real" surface. The anomalous isotope effect in the permeation of suprathermal gas also should manifest itself on other metals with a realistic surface composition, since the strong dependence of permeation on chemical composition of the surface is a universal feature of non-equilibrium gas–metal systems [4].

4. CONCLUSIONS

Isotope effects for H vs. D in factors of 20, $\sqrt{40}$ and 40, respectively, were observed in plasma driven permeation, retention, and in the reemission, at the interactions of Nb with H and D plasmas within a narrow range of bias voltages (40–80 V) at the lowest metal temperature investigated (910 K). The phenomenon occurred at the "superpermeation" of suprathermal hydrogen arising from an oxygen monolayer at the metal surface. The phenomenon is supposed to be due to the oxygen monolayer dynamics under the action of ion sputtering and surface segregation of dissolved O. Such and even much stronger isotope effects are also expected on other metals having a similar "real" surface. This isotope effect should be taken into account at consideration of D/T-mixture recycling, retention and permeation at its interactions with plasma facing components of fusion reactors as well as at the applications of superpermeable membranes for pumping of hydrogen isotopes and their separation from He.

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