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Journal of Nuclear Materials 290–293 (2001) 57–60

journal of nuclear materials

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Membrane bias effects on plasma-driven permeation of hydrogen through niobium membrane

A. Busnyuk [a,*], Y. Nakamura [a], Y. Nakahara [a], H. Suzuki [a], N. Ohyabu [a], A. Livshits [b]

[a] *National Institute for Fusion Science, Oroshi, Toki 509-52, Japan*
[b] *Bonch-Bruyevich University, 61Moika, St. Petersburg 191186, Russian Federation*

Abstract

Niobium membrane modeling a pumping system in the divertor region of a fusion plasma machine was immersed in hydrogen plasma in order to study interaction of the membrane with hydrogen ions in the energy range from a few eV to 200 eV, controlled by changing the membrane bias voltage. Bombardment by ions of an energy higher than 50 eV resulted in a decrease of the plasma-driven permeation/retention and in an enhancement of the boundary processes of absorption/reemission of thermal molecules. At ion energies below 50 eV, the effect of ion bombardment on plasma driven permeation and on the kinetic coefficients of boundary processes was non-monotonic in ion energy having a maximum at 10 eV. Both dissolution of oxygen in the membrane and increase of membrane temperature lead to diminution of the bias effect due to rise of recovering rate of surface impurity layer. © 2001 Published by Elsevier Science B.V.

Keywords: Plasma-driven permeation; Niobium; Sputtering; Surface segregation

1. Introduction

Permeation of hydrogen through membranes of the V_a Group metals is governed by recombination of absorbed hydrogen at the membrane surfaces over wide ranges of membrane thickness, temperature and incident flux density [1]. In the case of interaction with suprathermal hydrogen, the probability of hydrogen permeation through a membrane at this permeation regime is determined by implantation coefficient, ξ, and hydrogen molecule sticking coefficients at the upstream and downstream surfaces (α_{up} and α_{down}, respectively) as follows [2]:

$$\chi_H = \xi \frac{\alpha_{down}}{\alpha_{up} + \alpha_{down}}. \quad (1)$$

Metal surface is typically covered with a non-metal monolayer (e.g., [3,4]). This film is effectively impeding the dissociative absorption in, and thus the permeation of thermal molecular hydrogen through, the membrane. Still *suprathermal* hydrogen particles possessing a kinetic or a chemical energy exceeding ~1 eV are able to pass through such layers to be absorbed in the metal with a probability, ξ, that does not depend on surface temperature and equals 0.1–1, depending on energy [3–5]. As it follows from Eq. (1), 5–100% of an incident flux of suprathermal particles permeates through the membrane in the case of a favorable membrane asymmetry ($\alpha_{up} < \alpha_{down}$), irrespective of membrane temperature and thickness ('Superpermeability' phenomenon [6]).

Due to the above, membranes made of the V_a group metals could be employed in fusion machines for D/T mixture pumping and separation from impurities [1,7,8]. One of the possible applications of the superpermeable membranes is a suggestion to employ such membranes for pumping of the suprathermal hydrogen particles existing in the divertor region [1,9]. One of key points for such an application is possible modification of the

* Corresponding author. Address: University of Tokyo, 22-2, Shirane Shirakata, Ibaraki, Tokai-mura, 391-1106, Japan. Tel.: +81-2928 784 57; fax: +81-2928 784 58.

E-mail address: busnyuk@tokai.t.u-tokyo.ac.jp (A. Busnyuk).

0022-3115/01/$ - see front matter © 2001 Published by Elsevier Science B.V.
PII: S0022-3115(00)00621-8

membrane upstream surface by energetic hydrogen particles that may result in degradation of superpermeability. In the first place, the 'permeation spike' phenomenon [10–12] may take place, viz., an initially high permeation flux may be then drastically falling because of the non-metal impurity layer being sputtered from the membrane upstream surface by hydrogen ions of an energy above the impurity sputtering threshold: if α_{up} increases to significantly exceed α_{down}, because of impurity layer sputtering, the permeation will drop due to an unfavorable asymmetry developing (see Eq. (1)). It was shown, however, that superpermeation of Nb membrane remains stable at the energy of incident ions below a threshold of physical sputtering of light impurities 50–70 eV [13]. One of the purposes of this work was to investigate the membrane interaction with ions in an energy range of a few eV to hundreds of eV. Of a particular interest is the energy range below the threshold of physical sputtering: one would expect no superpermeability degradation in the absence of physical sputtering.

It was demonstrated that despite sputtering, a *stable superpermeation* through membranes of Nb [11,12] and stainless steel [11] was observed with ions *on a keV* energy scale when the upstream side was exposed to residual or specially admitted chemically active gases (O_2, H_2O, C_2H_2 or H_2S) that dynamically restore a non-metallic monolayer. The process of surface segregation of impurities also may play an important role in restoration of the surface impurity layer sputtered by energetic particles. Thus another purpose of this work was to investigate the effects of a simultaneous action of ion bombardment and of the surface segregation of non-metallic impurities (e.g., of O) on the plasma-driven permeation (PDP) through niobium membrane. In particular, it is important to study how the surface segregation might help to maintain superpermeation under sputtering.

2. Experimental

Hydrogen plasma surrounded a resistively heated tubular Nb membrane of 30 mm diameter, 150 mm length, and 0.3 mm thickness as shown in Fig. 1. An axis-symmetric hybrid-type plasma generator comprises an auxiliary hot-cathode duopigatrone plasma source and a Penning cell placed in transverse electric and magnetic fields. A typical discharge current and voltage are 3 A and 100 V, respectively, at hydrogen pressure $\sim 10^{-2}$ Torr. It produces cylindrically shaped plasma with electron temperature in a few eV and electron density in the range of 10^9–10^{10} cm^{-3}. A cylindrical water cooled shield made of stainless steel confines the plasma from the outside; it is kept under a floating potential. Two main groups of suprathermal hydrogen particles were impinging on the membrane: thermal atoms (typically $(5–10) \times 10^{16}$ H/(cm^2 s)), and ions

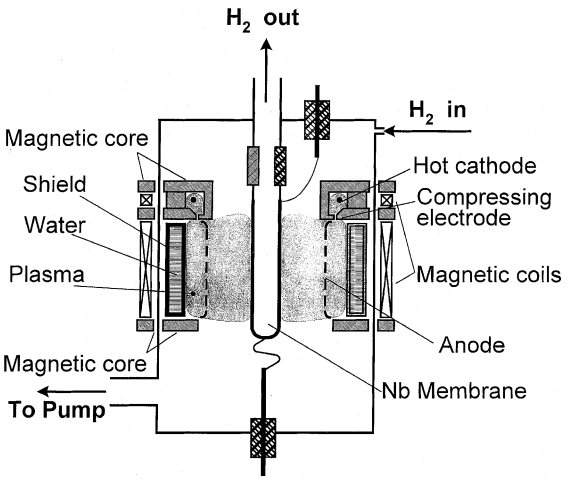

Fig. 1. Schematic of the experimental apparatus.

($\sim 3 \times 10^{15}$ cm^{-2}/s mainly H_2^+, H_3^+). The ion energy was controlled with biasing the membrane relative to plasma (practically, relative to the anode).

The device is designed as an ultra high vacuum (UHV) one. The whole device was baked at 250°C. Its upstream and downstream chambers are continuously pumped by two turbo molecular pumps through calibrated diaphragms (100 and 26 l/s for H_2, respectively), which allows to measure the permeation flux. Sticking coefficient of H_2 molecules at membrane upstream surface could be evaluated by 'compression' method [13]. A differentially pumped quadrupole gas analyzer indicated the partial pressure of impurity gases (mainly CO, H_2O) did not exceed 10^{-5} Torr during the plasma operation. Membrane temperature was measured with a thermocouple.

Heating of an Nb sample in UHV at $T \geqslant 600$°C results in the dissolution of original thick oxide film, with only a monolayer film remaining at the surface [3,12,13]. An AES analysis shows that this film usually consists of O and C. Oxygen was segregating back onto the surface from metal bulk after the surface has been exposed to an Ar^+ ion bombardment followed by heat treatment in UHV. Extra O could be introduced into the sample by means of its heating at 800°C at O_2 pressure of 2×10^{-4} Torr in the upstream chamber (at its permanent pumping). Heating of membrane resulted in a pronounced decrease of O_2 pressure. That allowed to estimate the amount of extra O absorbed.

3. Results and discussion

3.1. Effects of ion energy

Effects of membrane biasing on steady-state permeation flux density, j^b_{PDP}, on upstream sticking coefficient,

α^{b}_{up}, and on recombination rate constant, $k^{b}_{r\,up}$, are presented in Figs. 2 and 3 (the upper index 'b' points out that the given value is related to the condition of bias operation). Qualitatively these results are similar to the obtained earlier using another type of plasma membrane device [13].

At negative bias voltage ($U_b < 0$), about 3×10^{15} ions/s (mainly H_2^+ and H_3^+) are reaching the surface (see the membrane–anode current vs. bias voltage plot in Fig. 2). The ion bombardment effects depend on ion energy.

Above 50 eV, PDP flux decreases with an increase of the ion energy, E, as shown in Fig. 2. That is a normal behavior which can be attributed to the physical sputtering of light impurities (O and C) from metal surface: the sputtering coefficient increases with an increase of energy of incident ions starting with a threshold energy of several tens eV and having a tendency to a saturation at the energy higher than a few hundreds eV [14].

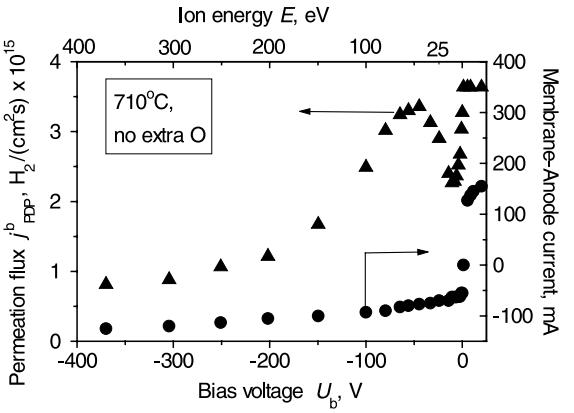

Fig. 2. Dependence of plasma driven permeation flux and membrane–anode current on the membrane bias voltage. Membrane temperature is 710°C.

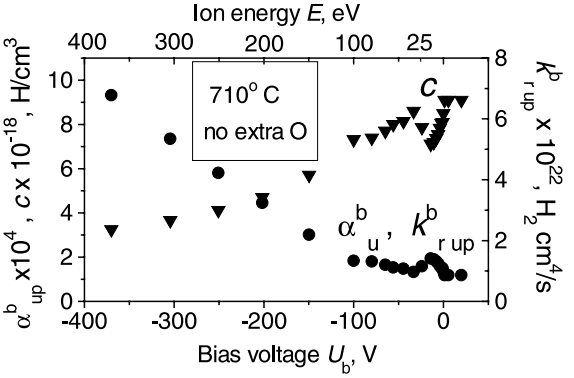

Fig. 3. Energy dependence of sticking coefficient, recombination rate constant and steady-state hydrogen concentration at 710°C.

Below 50 eV, j^{b}_{PDP} shows a complex behavior, with a minimum appearing at $E \approx 10$ eV. This phenomenon cannot be associated with an energy dependence of ion implantation/reflection coefficient, because the observed PDP was determined by neutrals (not ions) with a *constant* energy (see Section 2). Thus that is the effect of the surface modification exhibiting a resonance character with respect to ion energy. According to Eq. (1), such a modification should change either the probability of implantation of thermal atoms, ξ, or the probability of absorption of thermal molecules, α^{b}_{up}, to produce the observed alteration of PDP flux. As shown in Figs. 2 and 3, the pattern of α^{b}_{u} (and of $k^{b}_{r\,up}$) behavior at $E < 50$ eV is nearly reciprocal to that of j^{b}_{PDP}. It can be concluded from the presented data, referring to Eq. (1), that alteration of α^{b}_{up} determines the behavior of $j^{b}_{PDP}(E)$ at $E < 50$ eV, ξ being virtually independent of E. This pattern of α^{b}_{up} behavior at ion energy lower than the threshold of a physical sputtering might be related to chemical processes. For instance, chemical sputtering of O from the surface monolayer may be supposed to occur (e.g., $Nb_mO_n + H_2^+ \rightarrow Nb_mO_{n-1} + H_2O$). It should be noted that compounds of Group V_a metals with O are extremely stable and cannot be thermally reduced either by molecular or by atomic hydrogen at any temperature [3,13,15]. Incidentally, the authors never happened to come across a reference to such a non-monotonic energy dependence of chemical sputtering.

In order to emphasize the effect of surface modification due to energetic hydrogen on hydrogen inventory, we are presenting in Fig. 3 the steady-state concentration, c, of absorbed H. The concentration was found by $c = \sqrt{7.2 \times 10^{15}/k^{b}_{r\,up}}(\mathrm{H/cm^3})$, where 7.2×10^{15} H_2/(cm² s) is the absorption flux density in the given experiment (i.e., double the PDP flux density j_p at a zero bias); c is the concentration that would have been established, if there had been no permeation.

3.2. Effects of extra oxygen and temperature on j_{PDP} and α_{up}

Proceeding from the assumption that surface segregation of the dissolved O might condition the maintenance of non-metallic monolayer under sputtering, an extra amount of oxygen has been introduced in situ in the Nb membrane. Two portions of extra oxygen (0.2%(at.) and 0.4%(at.)) were successively introduced into the membrane. As expected, the effect of sputtering on PDP at $E > 50$ eV is decreasing with an increase of the oxygen concentration (Fig. 4). The amplitude of the minimum at $E > 50$ eV on the E dependence of permeation is also substantially reduced due to the extra oxygen. Also presented in Fig. 4 are the effects of oxygen and of bias on steady-state hydrogen concentration, c^b, normalized to the concentration at zero bias $(c^b/c^0)^2$.

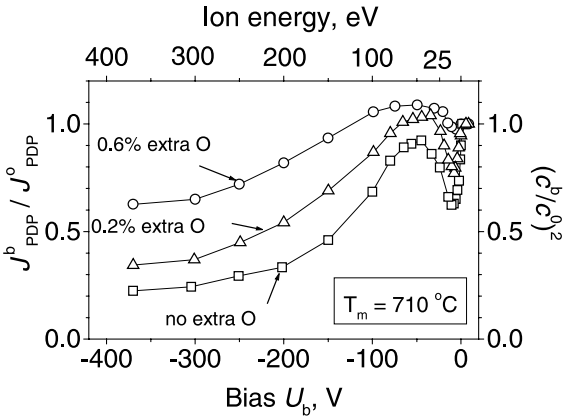

Fig. 4. Effect of extra oxygen on the bias dependence of PDP flux, j^{b}_{PDP}, normalized to the flux at floating potential j^{0}_{PDP}.

Thus both the permeation and retention of hydrogen (tritium) may be critically dependent on the dynamics of a monolayer covering the plasma facing surface.

The metal *temperature* is believed to be another factor that may assist in restoring of the oxygen monolayer, as the rate of O transport strongly depends on temperature. Thus, Fig. 5 shows that the effects of bias on the PDP flux, j_{PDP}, and on the sticking coefficient, α^{up}, (and hence on c) are rather strong at relatively low temperature but virtually disappear when temperature is high enough. Similarly to the effects of oxygen (Fig. 4), the influence of temperature is, at least qualitatively, the same for the two bias ranges (>50 V and <50 V). Fig. 5 shows, in particular, that the surface segregation is capable of maintaining the superpermeation under sputtering at high enough the membrane temperatures. Thus dissolution of oxygen may be contemplated as a practical way to secure the operation of a superpermeable membrane in the divertor of fusion devices, including low recycling (high temperature) regimes when the energy of incident particles may reach a few keV [9].

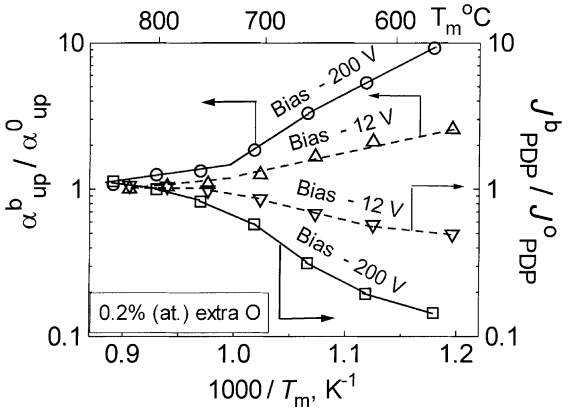

Fig. 5. Temperature dependence of upstream sticking coefficient and PDP at different energies of bombarding ions (biases) for the case when 0.2%(at.) extra O is dissolved; upstream sticking coefficient and PDP flux normalized to their magnitudes at zero bias.

4. Conclusions and acknowledgements

- Bombardment by hydrogen ions with $E > 50$ eV caused a reduction of the plasma-driven permeation/retention and an acceleration of thermal absorption/desorption. The reason for that is physical sputtering of the non-metallic monolayer which was dynamically maintained by the surface segregation of impurities (mainly O).
- At an ion energy below 50 eV, the plasma-driven permeation and boundary kinetic coefficients were non-monotonic in energy. Such a pattern of behavior seems to be rather intriguing and its cause is not quite clear (at least it hardly may be explained by only chemical sputtering).
- Both an in situ dissolution of extra O in Nb bulk and an increase of temperature were reducing the effects of ion bombardment due to maintaining of O monolayer. The surface segregation of non-metallic impurities may be a way of keeping up superpermeation under sputtering.
- The results demonstrate the important role that the dynamics of chemical state of surface may play in the D/T recycle, inventory and permeation in the plasma facing components in fusion devices.

This work was supported by ISTC under the project #1110.

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