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Effects of thin films on inventory, permeation and re-emission of energetic hydrogen

N. Ohyabu [a], Y. Nakamura [a], Y. Nakahara [a], A. Livshits [b,*], V. Alimov [b], A. Busnyuk [b], M. Notkin [b], A. Samartsev [b], A. Doroshin [b]

[a] *National Institute for Fusion Science, 322-6 Oroshi-cho, Toki, Gifu-ken, Japan*
[b] *Bonch-Bruyevich University, 61 Moika, St. Petersburg 191186, Russian Federation*

Abstract

A non-metallic coating thicker than the implantation depth may protect a metal against tritium retention and permeation. However, a thinner film has quite the opposite effect: a *dramatic increase* of permeation and retention, and a corresponding suppression of re-emission. In view of the benefits expected from particle control with a superpermeable membrane placed right inside the divertor, the behavior of a Nb sample was investigated in a plasma-membrane device having a graphite target. Even polyatomic carbide coating was found not to hinder hydrogen absorption and permeation. Polyatomic non-carbide C films effectively inhibits it, but the formation of such films depends on H and C fluxes, H energy and metal temperature. A durable isolation of suprathermal hydrogen with the superpermeable membrane was observed at a high enough ratio between H and C fluxes, and the effects of carbon were found to have a non-monotonic temperature dependence. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The presence of thin non-metal films on a plasma-facing metal surface has been shown to play a crucial role in the metal interaction with suprathermal hydrogen particles [1–3]. If the film is thinner than the implantation depth, then it is capable of increasing by orders of magnitude the absorption and permeation capabilities of the metal with respect to energetic hydrogen through suppressing of the re-emission of the absorbed hydrogen. Two implications important for fusion follow from this.

First, the properties of plasma-facing materials (PFM) that govern re-emission, absorption and permeation depend on the physico-chemical environment. Thus, the PFM behavior in fuel re-cycling and tritium inventory/permeation may be dramatically changed during the operation, and such an evolution is not easily predictable.

Second, the effects of thin non-metallic films allow for the manufacture of special materials possessing an enhanced absorption and superpermeation that can be employed for a short-way separation of D/T from He [4] and for an active particle control in fusion devices (pumping, special flow loops, etc.) [5].

We will briefly present the underlying ideas about the role of thin coatings. Then, we will consider an experiment with a Nb sample (membrane) exposed to concurrent fluxes of hydrogen particles and carbon (under conditions modeling the membrane operation in a divertor zone).

2. A peculiar role of thin non-metallic coatings at PFM interaction with suprathermal gas

The rates of absorption in metals of *thermal* H_2 molecules, j_{ab}^{e}, and of the evolution of absorbed atoms, j_r, are [6,7]

$$j_{ab}^{e} = \alpha_0 j_{in} = \alpha_0 z p, \quad j_r = k_{r0} c^2, \tag{1}$$

where j_{in} is the incident flux density, z the kinetic theory coefficient, p the pressure, α_0 the probability of the

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[*] Corresponding author. Tel.: +7-812 587 9921; fax: +7-812 587 9334.
E-mail address: livshits@mail.axon (A. Livshits).

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dissociative binding of H_2 per single impact (the sticking coefficient), k_{r0} the re-combination rate constant, and c is the concentration of absorbed gas. At equilibrium, $c = c_e$ [8] and

$$c_e = S\sqrt{p} = S\sqrt{\frac{j_{in}}{z}}, \tag{2}$$

where S is the solubility constant. From Eqs. (1) and (2) it follows:

$$k_{r0} = \frac{\alpha_0 z}{S^2}. \tag{3}$$

One can see that only the absorption/evolution kinetics, and not the *equilibrium* concentration, depends on characteristics of the surface (α_0). However, the situation is different in the case of an *energetic* gas: the rate of absorption in metal, j^s_{ab}, is given by

$$j^s_{ab} = \xi j_{in}, \tag{4}$$

where the probability of absorption *in metal*, ξ, is, unlike α_0, temperature independent and may be insensitive, in the first approximation, to the presence of a thin non-metallic film whose thickness is less than the implantation depth; in the case of fast particles, ξ is the implantation coefficient. The re-emission of absorbed hydrogen may still remain a thermal process even at low temperatures such as 300–400 K [9,10]. Hence the *steady-state concentration* c_{qe} becomes *dependent on surface characteristics*, rising with decreasing α_0

$$c_{qe} = c_e\sqrt{\frac{\xi}{\alpha_0}}. \tag{5}$$

(Eq. (5) is obtained from the balance $\xi j_{in} = k_{r0}c^2_{qe}$ by accounting for Eqs. (2) and (3).) In the same manner, the permeation flux, j_{ps}, rises with decreasing α_0 in the case of an *energetic* gas (α_0 refers to the membrane upstream surface): in the case of a thick enough membrane,

$$j_{ps} = \frac{D}{L}c_{qe} = \frac{D}{L}c_e\sqrt{\frac{\xi}{\alpha_0}}, \tag{6}$$

where D is the diffusion coefficient and L is the membrane thickness. At certain conditions (in particular, if α_0 is sufficiently small) [6,7], j_{ps} starts being governed only by the implantation coefficient and the membrane asymmetry factor, α_L/α_0 (where α_L is a sticking coefficient at the downstream surface)

$$j_{ps} = j_{in}\xi\frac{1}{1 + (\alpha_0/\alpha_L)}. \tag{7}$$

At $\alpha_L/\alpha_0 > 1$, almost the whole implanted flux passes through the membrane depending neither on membrane temperature nor on thickness (superpermeability [1,3,4,6,7,10,12–15]).

Thus, k_{r0}, c_{qe} and j_{ps} depend on α_0; the latter may be presented as

$$\alpha_0 = (0.1 - 1)\sigma_0 \exp - (2E_{r0}/RT), \tag{8}$$

where σ_0 is a part of the surface occupied by the active centers of thermal absorption/desorption characterized by potential barrier E_{r0}. In the case of a *clean* surface of transient metals, $\sigma_0 \approx 1$, $E_{r0} = 0$, and $\alpha_0 = 0.1$–1 [11]. Still a metal surface usually would be covered with either a monatomic (very typically [1,3,12]) or a thicker non-metallic film. The film gives rise to a barrier ($E_{r0} \gg RT$) and a surface non-uniformity ($\sigma_0 \ll 1$), so that α_0 may vary over orders of magnitude depending on T as well as on the type of coating and metal [3]. Therefore, thin overlayers would result in a drastic increase of c_{qe}, j_{ps} and a decrease in k_{r0}. If the energy of the incident hydrogen is lower than ≈50 eV, then the overlayers (and α_0) may remain unchanged [2,10], whereas at a higher energy the coating characteristics (and hence the magnitudes of α_0, k_{r0}, c_{qe} and j_{ps}) may be drastically changed, depending on the balance between coating sputtering and restoration (sputtering may be counterbalanced, e.g., by the deposition of impurities or their surface segregation) [2–4,10,13].

3. Experiment

The above effects have been obtained on a number of coatings and substrates in a wide hydrogen energy range (e.g., [1–4,10,12–15]). The goal of this experiment was to investigate the effects produced by carbon being deposited onto a Nb membrane sample during its interaction with energetic hydrogen and, in particular, to model the operation of a superpermeable membrane located in the divertor zone of the Large Helical Device [16].

3.1. Experimental setup

A hydrogen plasma surrounded a resistively heated tubular Nb membrane of 1.5 cm diameter, 15 cm length, and 0.2 mm wall thickness. The plasma ($n_e = 10^9$–10^{10} cm^{-3}, T_e in a few eV, $p \approx 10^{-2}$ Torr) was generated by a discharge (3 A × 80 V) with a hot W cathode. It had the shape of a hollow cylinder (Fig. 1) and was confined by a magnetic field mainly in the space between a target and a grid anode. A resistively heated partly transparent grid target (56 cm^2) made of graphite contacted the plasma, surrounding it from the outside. A cylindrical Mo shield was placed behind the target. Two main groups of suprathermal hydrogen particles impinged on the membrane: thermal atoms (typically $\sim 5\times10^{16}$ H/(cm^2 s)) and atoms originating from ion neutralization at the target. The average energy of the latter may have been controlled by target biasing, while

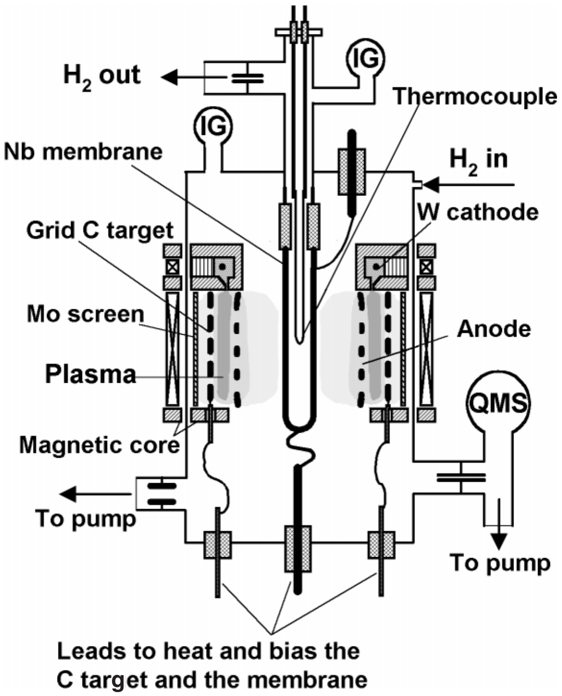

Fig. 1. Schematic of the experimental device.

their flux estimated from the ion current and reflection coefficient typically was 10–20 times smaller than the flux of thermal atoms. An additional flux of energetic ions ($\sim 3 \times 10^{15}$ (H_2^+, H_3^+)/(cm^2 s)) could have been obtained by membrane biasing. Furthermore, thermal atoms may have been generated without plasma at hot cathode filaments.

The ultra-high vacuum (UHV) device's upstream and downstream chambers are continuously pumped by two turbo-molecular pumps through calibrated diaphragms (100 and 30 l/s for H_2, respectively), which permit measuring the permeation flux. A differentially pumped quadrupole gas analyzer permits measuring the mass spectra during plasma operation.

Nb sample heating in UHV at $T > 600°$ C results in the dissolution of the original thick oxide film, with only a monolayer film remaining [3,12]. The Auger electron spectroscopy analysis shows that this film usually consists of O and C [12]. If the C flux onto the surface is negligible, then the film keeps stable under suprathermal hydrogen particles of an energy of up to a few tens of eV [2,13] with no special efforts needed to maintain the membrane superpermeability to such particles [13].

3.2. Experimental results and discussion

3.2.1. Carbon flux

In the presence of a C target, even thermal H atoms produce carbon species: we observed CH_4 directly, and CH_3 radicals must be generated with approximately the same rate [17]. We were varying the fluxes of hydrocarbons and C atoms over wide ranges in our experiment, with selectable predominance of one species by controlling the target bias and temperature [17]. To find the flux of C deposited onto the membrane from hydrocarbons, we assumed all the CH_3 formed to be sticking uniformly over the plasma-facing surfaces (whereas the major part of CH_4 was found to have been pumped).

3.2.2. Effect of membrane temperature on C film growth

With only the cathode on, superpermeability to thermal hydrogen atoms with a typical *temperature independence* of j_{ps} (Section 2) was observed (Fig. 2) and *was quite stable in spite of the C flux*. Therefore, chemical sputtering prevents the formation of polyatomic C film, the original monolayer remaining responsible for the interface processes.

A stable temperature independent *plasma-driven* permeation (superpermeation) was also observed at relatively low C fluxes (Fig. 2). At higher C fluxes, the ability of the plasma-facing surface to withstand the growth of polyatomic C films depends on *T*. This was demonstrated as follows (Fig. 3). The membrane underwent isochronal (1.5 h) plasma exposures at different *T*. After every exposure, the state of the surface was examined at a standard temperature of 520°C by the atomic-driven permeation (ADP) due to the hot cathode. Before exposure at the next *T*, the standard state of the membrane (including the ADP magnitude) was restored by heating for a few minutes at 1200°C.

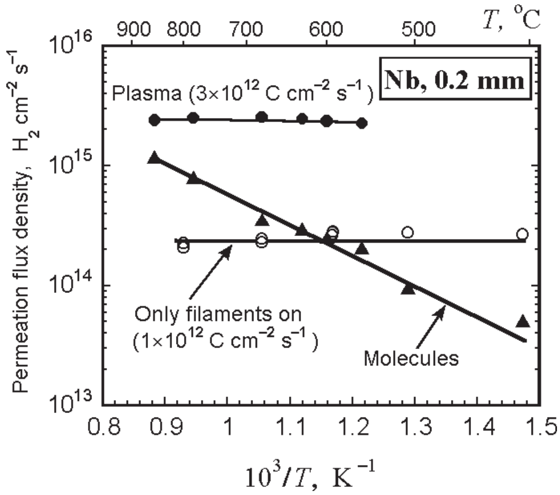

Fig. 2. Temperature dependence of molecule-, atom- and plasma-driven permeation in the presence of a flux of carbon (as indicated in the brackets). In the case of plasma, the membrane and target are at a floating potential.

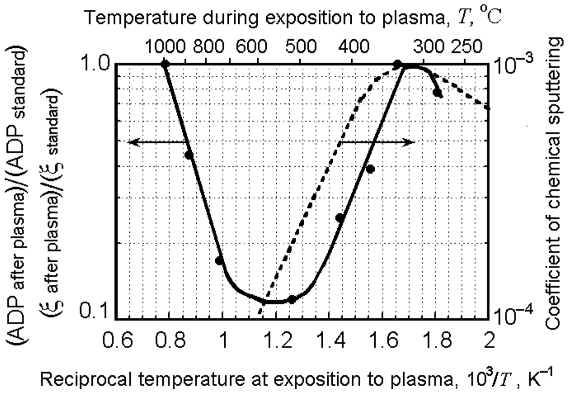

Fig. 3. Effects of the isochronal (1.5 h) membrane exposures to a C-contaminated H plasma (C flux ~ 10^{13} cm^{-2} c^{-1}) on the permeation of thermal atoms (ADP) and on the probability of their absorption, ξ, as functions of membrane temperature during the exposure. The coefficient of chemical sputtering [17] by thermal H atoms of the deposited C film is also presented (thermal H atoms were mainly responsible for sputtering under plasma, as explained in the text, since the target and membrane were under a floating potential in this experiment). ADP served as a gauge for the presence of polyatomic C film. ADP has been measured at one and the same temperature (520°C) before and after the exposures to plasma at every given T.

In the case of Nb, j_{ps} is always determined by Eq. (7) [3,13], and the observed ADP reduction may originate from either a decrease of the asymmetry factor, α_L/α_0, or a decrease in the probability of absorption of thermal H atoms, ξ. The asymmetry was shown not to be decreasing [13], whence it was the growth of a polyatomic film barring the absorption of atoms that was responsible for the effect of plasma. The low-temperature branch of the graph in Fig. 3 may be associated with the chemical sputtering of C by thermal H atoms [17], while the high-temperature branch with the diffusion of C into metal producing a bulk carbide that does not hinder hydrogen absorption (see below). Thus, it is easier to prevent the growth of polyatomic (not carbide) C films at a relatively low or a relatively high temperature. Still a low temperature has the advantage that C is not accumulated.

3.2.3. Effects of target and membrane biasing

In the next experiment (Fig. 4), a 300 V bias relative to the plasma was applied to the target after the establishment of plasma-driven permeation; with 170 mA of H_2^+ and H_3^+ ions hitting the target, biasing produces a flux of ~6×10^{13} C/(cm^2 s) of physically sputtered C atoms onto the membrane (taking 1×10^{-2} for sputtering coefficient [18]). Even though energetic reflected H atoms (~3×10^{15} H/(cm^2 s), 50–100 eV) were getting at the membrane alongside C, permeation started decreasing due to the ξ decrease that occurs with the growth of polyatomic C film, as the deposition of C surpasses its removal (a special test showed the asymmetry α_L/α_0 not to be decreasing). To intensify C removal with no damage to the O monolayer [13], a low-voltage bias was applied to *the membrane*, so that the energy of ions falling onto the membrane from the rare plasma surrounding it (~3×10^{15} H_2^+, H_3^+)/(cm^2 s) rose to a few tens of eV. As a point of fact, the permeation decrease gave way to its rise, and a stable permeation was reached and maintained during the whole observation time. [1] About 10^3 C monolayers might have been deposited during that time; had that actually taken place, such a film would have been virtually impenetrable to all groups of H particles.

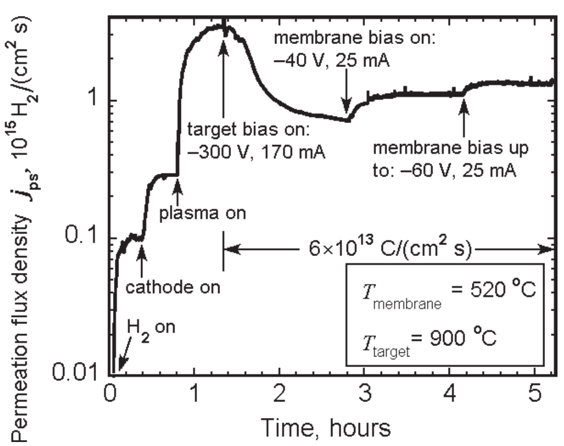

Fig. 4. The evolution of plasma-driven permeation caused by the target and the membrane bias. Biasing the target results in a dramatic carbon flux increase, with physically sputtered C atoms (6×10^{13} C/(cm^2 s)) dominating over chemically sputtered hydrocarbons due to a high (900°C) target temperature [17]. Besides, biasing of the target gives rise to a flux (~3×10^{15} H/(cm^2 s) of energetic (50–70 eV) reflected H atoms bombarding the membrane.

3.2.4. The role of carbides of the group Va metals

Membrane heating at $T = 1000$–1200°C was usually employed to restore the state of superpermeable membrane to superpermeability after C deposition. Carbon will not be removed from the sample at such temperatures, and therefore it must be diffusing into the bulk metal. Thousands of C monolayers would be transported in this way inside metal during a typical experimental campaign to exist only in the form of carbide there (C solubility in Nb is negligible [8]). In fact, a

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[1] However, permeation was not completely restored with biasing the membrane. The most likely explanation is that the tubular membrane stands out of the plasma (Fig. 1) and is being only partly sputtered.

layer-by-layer AES analysis of extracted samples revealed a 1 μm (!) near-surface NbC/Nb_2C layer. So one has to conclude that, unlike the modifications of pure C (graphite, a:C-films, diamond-like films), *NbC* (*and perhaps VC, TaC as well*) *do not stop hydrogen transport in the superpermeation regime*. Hence: (1) the surface barrier inhibiting hydrogen re-emission remains as Nb transforms into NbC (perhaps due to an oxicarbide monolayer), and, (2) a very large magnitude of $D \times S$ inherent to Nb is conserved in NbC.

4. Conclusions

- Thin non-metallic coatings may drastically increase hydrogen absorption and permeation and suppress re-emission during metal interaction with suprathermal hydrogen.
- The capability of Nb having a natural surface O monolayer to withstand the growth of polyatomic C films and to retain superpermeability is governed by the ratio of C and H fluxes and is non-monotonic in temperature dependence.
- Polyatomic films of NbC/NbC_2 were found not to hinder Nb superpermeation.

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