ELSEVIER

Journal of Nuclear Materials 266–269 (1999) 1267–1272

journal of nuclear materials

Fuel recycling and edge plasma control with membrane techniques: plasma–membrane simulation experiments

A. Livshits [a,*], N. Ohyabu [b], M. Bacal [c], Y. Nakamura [b], A. Busnyuk [a], M. Notkin [a], V. Alimov [a], A. Samartsev [a], H. Suzuki [b], F. Sube [c]

[a] *Bonch-Bruyevich University, 61 Moika, St. Petersburg 191186, Russian Federation*
[b] *National Institute for Fusion Science, 322-6 Oroshi-cho, Toki, Gifu-ken 509-52, Japan*
[c] *LPMI, Laboratoire du CNRS, École Polytechnique, 91128 Palaiseau, France*

Abstract

Membranes of Nb and V were examined with the use of a few plasma devices simulating different fusion machine conditions. A reproducible long-time plasma driven superpermeation was observed at all the flux densities up to 2×10^{17} H cm^{-2} s^{-1} at membrane temperatures, T_m, 500–1000°C. The deposition of stainless steel components on the membrane upstream surface resulted in a permeation drop at $T_m < 750$°C, though the membrane annealing at $T_m \geqslant 750$°C restored superpermeation. A superpermeable membrane in combination with *He plasma* was shown to be a suitable means to isolate hydrogen impurities from He.

Keywords: Membrane pumping; Plasma-driven permeation; Hydrogen recycling; Divertor pumping; Niobium; Vanadium

1. Introduction

A metallic membrane of macroscopic thickness may be *superpermeable* to hydrogen particles whose energy (kinetic, internal or chemical) exceeds ~1 eV [1]. This means that virtually the whole flux of suprathermal particles implanted in the metal lattice, or just sticking to its surface, passes through the membrane, with the permeation flux depending neither on the membrane temperature nor on its thickness. When the incident energy is 1 keV or higher, the implantation probability is close to unity. Therefore almost the whole *incident* flux permeates through the membrane and the permeability of a solid membrane approaches unity too. At lower energies (including thermal atoms), a fraction of the incident suprathermal particles can be reflected back from the surface; still the probability of implantation (sticking) stays comparable to unity (typically $\geqslant 0.2$) even in this case, as also does the permeation probability. Since the implantation/sticking probability for low energy suprathermal particles does not depend on the metal temperature, the corresponding permeation flux should also be temperature independent at superpermeability.

A superpermeable membrane can automatically compress the permeating gas by orders of magnitude and separate it from any impurities, including He. The phenomenon was investigated with thermal hydrogen atoms and fast (>70 eV/H^+) ions using the atomic and ion beam techniques. Membrane systems comprising a superpermeable Nb membrane and a hot metallic surface to atomize H_2 molecules were investigated and technologically developed for possible fusion applications [2–4]. Still membrane systems combined with plasma serving as a source of energetic hydrogen seem to be more promising for a number of reasons [5,6], and thus the efforts of research groups in Japan, France and Russia were focused in the last years on attempts to obtain and investigate plasma driven superpermeation.

2. Possible applications in fusion

According to the above, superpermeable membranes may be employed: (1) to *separate D/T fuel and He ashes*

* Corresponding author. Tel.: +7 812 314 6659; fax: +7 812 315 7610; e-mail: livshits@qrel.sut.ru

0022-3115/99/$ – see front matter
PII: S0022-3115(98)00693-X

in fusion device exhausts, with the aim of decreasing tritium accumulation and improving safety [2–5], (2) to *pump and recirculate D/T*, with the aim of improving *the edge plasma and divertor performance* [3,7], (3) to *pump and/or recuperate D/T in auxiliary systems* (pellet and neutral beam injectors, etc.).

A technique of short-way isolation of a D/T mixture from tokamak exhausts was suggested employing a superpermeable membrane installed along the walls of pumping ducts leading to the cryogenic pumps serving to pump He [2–4]. For instance, the data of our simulation experiments with thermal H atoms permit to conclude that the tritium load on cryopumps might be decreased by orders of magnitude in the case of ITER with a membrane system of reasonable size combined with an incandescent metal surface to produce H atoms. There are at least two reasons why the employment of plasma as a source of energetic hydrogen would appear rather attractive for this application. First, a membrane panel might be placed in the divertor plate vicinity [2], and in this case one can make use of energetic hydrogen generated in the divertor plasma. On the other hand, the membrane might be placed in the pumping duct at some distance from the divertor [2–4] in order that the membrane performance did not depend on unpredictable divertor plasma conditions. In the latter case, an additional generator of energetic hydrogen particles is required; arranging of a special gas discharge might be simpler in design and more energetically effective than the atomization on a hot surface (e.g., in the case of ITER the hot atomizer will consume 0.05 to 5 MW, depending on pumping regimes [4], more than 99% of which will be wasted on radiation). It is also expected that D/T evacuation with a membrane will result in so high a He enrichment that D/T may become a small impurity in He, and thus a discharge in He (not in hydrogen) must be simulated in view of this application.

Another proposal [3,7] refers to the Large Helical Device (LHD) that was put into operation in Japan recently. Specifically, the suggestion consists in pumping out the LHD divertor region of at least 70% of the incoming hydrogen flux in order to provide for the high-temperature divertor plasma operation [8] which is expected to result in a substantial temperature rise of the main plasma. Besides, such pumping must be a *steady-state* process to concur with the steady-state operation of the helical device. For these reasons, *plasma driven superpermeation* is considered as a promising way to pump hydrogen in LHD, even though no tritium is planned to be used there.

Finally, a proposal has been put forward to use superpermeable membranes for hydrogen pumping in the plasma neutralizer of negative hydrogen ions in neutral beam injectors (in particular, in the LHD) [8].

3. The role of surface chemistry

A monolayer nonmetal film on the upstream surface of a metallic membrane is responsible for superpermeation [1,2], and the main practical point is *getting a stable long-term operation of superpermeable membranes regardless of the effects of plasma* on the upstream surface. There are two factors acting in the opposite directions that may lead to superpermeability degradation: a growth of nonmetallic films substantially *thicker than a monolayer*, and damage, or even a complete removal, of the monolayer films. The first factor gains particular importance in the plasma–membrane systems where chemical radicals are inevitably formed in hydrogen plasma in the presence of carbon- and oxygen-containing impurities. On the other hand, the surface films can be either physically sputtered by energetic particles or (even though many nonmetallic *monolayer* films turn out to be absolutely stable under the action of *thermal* atomic hydrogen [2–4]) removed by way of chemical sputtering with hydrogen particles of an energy in the range of one to tens of eV (including the Frank–Condon atoms).

Nevertheless, a surface covered with a monatomic nonmetallic film in vacuum is typically a natural state of the metal surface in thermodynamic equilibrium, viz., there are mechanisms that *automatically* maintain a more or less monatomic coverage through either removing the excessive atoms via their dissolution in bulk metal or replenishing the missing ones via surface segregation and reactions with the ambient gases [4,9]. Thus the question is whether or not the ability for self-maintenance of the surface of a superpermeable membrane will suffice to ensure stable long-term operation of the superpermeable membrane under plasma conditions.

4. Experimental

The plasma driven permeation was experimentally studied with using three different plasma device schemes (Fig. 1) to simulate the operation of the membranes in fusion machines in different situations. In all the three cases, the membranes were made of the Group Va metals: Nb or V. Auger electron spectroscopy (AES) of the membrane material showed O and C as the main impurities on the surfaces of the both metals. With our AES analysis accuracy, these impurities formed monolayer coatings after heating (>550°C) in vacuum ($\approx 10^{-10}$ Torr) inside the Auger spectrometer. The same impurities were again discovered after the surfaces cleaned up with an Ar^+ ion bombardment in the ultra-high vacuum of Auger spectrometer chamber had been again heated in situ up to >550°C (a typical manifestation of the segregation of bulk nonmetallic impurities onto the metal surface [9]). The same was found with AES

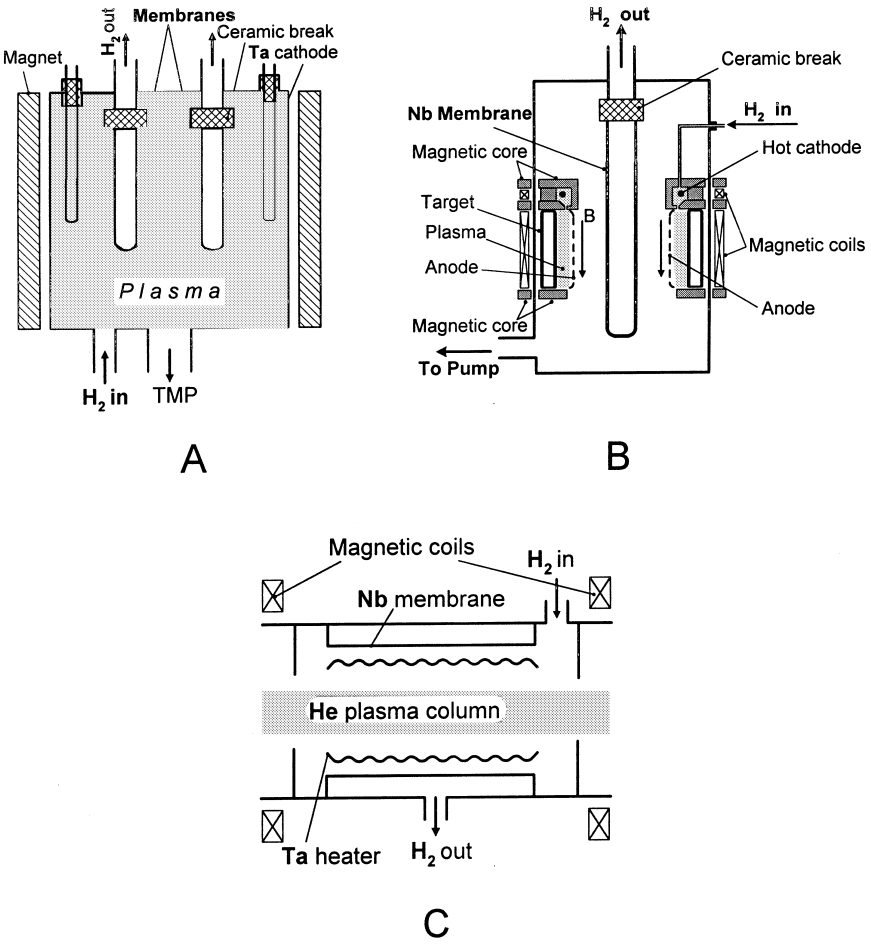

Fig. 1. Three schemes of plasma membrane experiment.

analysis of the membrane upstream surfaces after their long-time operation in plasma in our devices.

In the Scheme A in Fig. 1 [5], two resistively heated tubular membranes (of Nb and V) of 1 cm diameter, 18 cm length, and 0.1 mm wall thickness were immersed into a uniform hydrogen plasma (plasma density, $n_e \approx 10^{10}$–10^{11} cm^{-3}, electron temperature, $T_e \approx 1$ eV, H_2 pressure $p_{H_2} = 10^{-3}$–10^{-2} Torr) generated by the discharge between Ta cathode filaments and the chamber wall in a multicusp magnetic field [10]. The incident ion energy could have been controlled by membrane biasing. Densities of ion flux up to 10^{16} cm^{-2} s^{-1} and of atomic flux up to 10^{18} cm^{-2} s^{-1} acting upon the membrane surface could have been obtained here. A continuous deposition of Ta from cathode filaments onto the membrane upstream surface is inevitable due to the device geometry (Fig. 1). Note that all the three metals, V, Nb and Ta, belong to the Va Group, and their chemical properties, particularly, the characteristics of their interaction with hydrogen, are basically similar [11]. That was the reason why we employed Ta as the filament material in Scheme A.

In the Scheme B, hydrogen plasma ($n_e = 10^9$–10^{10} cm^{-3}, T_e in a few eV, $p_{H_2} \approx 10^{-2}$ Torr) generated by the discharge with a hot W cathode had the shape of a hollow cylinder. Importantly, the hot tungsten cathode is carefully hidden from a direct line of sight with both the membrane and the target; an AES analysis discovered no W traces outside the cathode-confining space [Fig. 1(B)]. The plasma surrounded a resistively heated tubular Nb membrane of 3 cm diameter, 15 cm length, and 0.3 mm wall thickness. The plasma contacts a cylindrical target surrounding it from the outside. Magnetic field confines the plasma mainly in the space between the target and the grid anode. The membrane is exposed to concurrent flows of the hydrogen neutrals produced at plasma neutralization at the target and of the sputtered target atoms. The flux and energy of hydrogen neutrals and the flux of target atoms were controlled with target biasing. For instance, at a target bias relative to the

plasma −500 V, the ion current density on the target is ≈10 mA cm^{-2} or (1–2) × 10^{17} H^+ cm^{-2} s^{-1}, with accounting for that the ion flux mainly consists of H_2^+ and H_3^+ ions. On assuming that about a half of incident ions is reflected from the target as fast H atoms, one gets (0.5–1) × 10^{17} H cm^{-2} s^{-1} for the H atom flux onto the membrane. Simultaneously, ≈10^{14}–10^{15} cm^{-2} s^{-1} of ion-sputtered target atoms will be deposited on the membrane. The scheme was to simulate the operational environment of a membrane placed at the line of sight with a divertor plate, with the main focus on the LHD divertor conditions.

In Scheme C, a cylindrical membrane (Nb, 12 cm diameter, 25 cm length, and 0.1 mm thickness) encircled a He plasma column of 1.5 cm diameter confined by a magnetic field ($n_e = 10^{11}$–10^{13} cm^{-3}, $T_e = 2$–10 eV, depending on the plasma source discharge current) [12]. The He plasma generates energetic hydrogen neutrals (mainly, Frank–Condon atoms) from specially introduced ambient hydrogen. A set of resistively heated Ta filaments served as the membrane heater. This scheme simulates the isolation of D/T from He in fusion reactor exhaust for the case when D/T becomes a small impurity in He due to an effective membrane evacuation. In all the three cases, the plasma side and the membrane downstream side were continuously pumped with turbomolecular pumps during the plasma membrane experiment. Still it was only the setup according to Scheme B (Fig. 1) that has been specially designed for the plasma–membrane experiments as an UHV system (taking into account the importance of the state of membrane surface [1,4]), while the other two plasma devices were unbakeable and were not oil-free. The plasma driven permeation was experimentally observed by following the hydrogen pumping effect [2]: the upstream pressure drops to a lower steady-state level and the downstream pressure correspondingly rises after switching on the plasma.

5. Experimental results and discussion

Evidence of plasma driven superpermeation: We are able to measure not only the permeation flux, j_p, but also the flux being absorbed, j_{ab}, (and thus their ratio, j_p/j_{ab}, too). For instance, we can establish steady-state plasma driven permeation at a relatively high membrane temperature, T_m, (e.g., 700–800°C) and then decrease T_m quickly. The thermal desorption gets temporarily stopped (including the upstream side reemission) while the absorption of suprathermal hydrogen which does not depend on T_m remains unchanged, resulting is a temporary additional pumping, and j_{ab} may be found easily this way. Such experiments yielded j_p/j_{ab} to vary from 0.5 to 0.9 in our plasma experiments at the membrane floating potential. This value is maintained at a negative membrane bias relative to the plasma, U_b, of up to −(50–70) V, and thus the major part of absorption flux permeates through the membrane.

It is only at a higher negative bias ($U_b < -(50–70)$ V) that the j_p/j_{ab} ratio starts decreasing due to the physical sputtering of monolayer nonmetallic films responsible for the superpermeability phenomenon [13]. Such a drop of permeation through an initially superpermeable membrane was also observed in the ion beam experiments at ion energies higher than 70 eV/H^+ [1,2]. Still there were means to restore and maintain the superpermeable regime in spite of the physical sputtering. For instance, admitting chemically active gases (O_2, H_2O, CH_4, H_2S) onto the membrane upstream side in the course of bombardment by an ion beam increases an extremely small steady-state ion driven permeation up to superpermeation, and the latter exists as long as a chemically active gas is present [1,2].

The permeation flux temperature independence is one of the most characteristic superpermeation properties [1]. One can see from Fig. 2 that *temperature independence of the plasma driven permeation is actually observed* at $T < 950$°C. At $T > 950$°C, the permeation flux drops with temperature increase because of the superpermeability degradation. It is a typical occurrence at a high enough metal temperature: the potential barrier at the upstream surface (formed by a nonmetallic film) ceases to effectively prevent the thermal reemission of absorbed atoms at higher temperatures [1], so the absorbed atoms start being reemitted back before they reach the membrane downstream side.

The plasma driven superpermeation remained quite stable and reproducible during hundreds of hours of operation (about 500 h) with the permeation fluxes (10^{15}–10^{17} H_2 cm^{-2} s^{-1}) and at the temperatures (550–950°C) where superpermeation has been initially observed. The maintenance of the required state of the membrane upstream surface demanded no special efforts

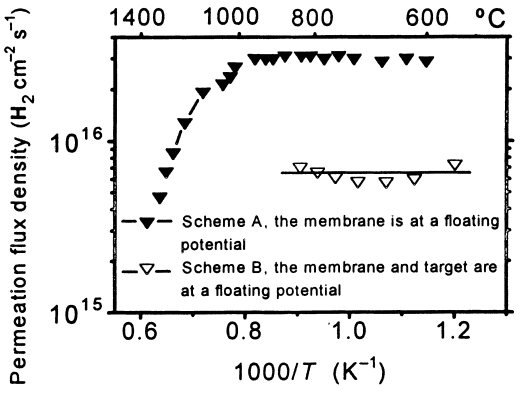

Fig. 2. Temperature dependence of plasma driven permeation through Nb membranes.

until the incident ion energy exceeded 50–70 eV. On the other hand, one could destroy the superpermeation in a controllable way, e.g., by sputtering of the monolayer nonmetallic film with membrane biasing below −70 V [13] (an in situ heating to $T > 550$°C restored superpermeation due to the segregation of nonmetallic impurities from bulk metal onto the surface). Vice versa, the growth of a *thick* carbon film when the plasma contained too much organic impurities resulted in the permeation drop by more than an order of magnitude. The latter occurred with Scheme A just after the plasma had been switched on for the first time with oil present on the vacuum chamber walls (the partial CH_4 pressure in the vacuum chamber rose from 10^{-8} to 10^{-6} Torr at the first discharge ignition). However, the content of organic species in the plasma substantially decreased in a few hours after the discharge initiation (with a discharge current 50 A and a voltage 65 V), and the permeation increased by more than an order of magnitude to acquire all the properties of superpermeation including the temperature independence (Fig. 2). After this initial stage, the superpermeation remained stable and reproducible.

Dependence on flux: It would be natural to assume the density of the incident flux of suprathermal hydrogen particles, j_i, to be proportional to the flux of primary electrons in the gas discharge that generates them, i.e., to the discharge current, I_d. Thus, $j_p \propto I_d$ should be expected at superpermeability. One can see from Fig. 3 that a proportionality to I_d is actually observed over the whole ranges of j_p and upstream pressures investigated [5]. An examination of every point on the graphs in Fig. 3 confirms the existence of the superpermeation regime: $j_p/j_{ab} > 0.5$, and j_p does not depend on T_m. So the plasma facing surface turns out capable of keeping up of a state that secures superpermeability at all the investigated flux densities in spite of the surface being continuously acted upon by suprathermal particles.

Remarkably, the j_p values presented here (up to almost 10^{17} cm^{-2} s^{-1}) exceed by orders of magnitude those reached with the particle beam techniques, and they are the record ones ever attained in superpermeability experiments. Thus a substantial progress has been achieved due to the employment of plasma as a generator of energetic hydrogen. Still technical reasons did not permit our advancing further up to higher fluxes even in this case, though the theoretical j_p limit amounts to a value of $\sim 10^{19}$ cm^{-2} s^{-1} for the superpermeation regime [4].

Effect of the deposition of other metals: Austenitic stainless steel (ASS) was chosen as the first target material in Scheme B (carbon materials are also supposed to be used in the nearest future). Temperature dependencies of the effects of ASS deposition on permeation and on the hydrogen recombination rate constant [1] at the membrane upstream side, k_{ru}, are presented in Fig. 4. The ASS deposition on the upstream surface at $T_m < 750$°C results in an easier back desorption from the upstream side: the ratio k_{rd}/k_{ru}, where k_{rd} and k_{ru} are the recombination rate constants for the upstream surface covered by ASS components and for the unchanged downstream surface respectively, becomes temperature dependent and less than unity. Correspondingly, superpermeation is destroyed [1], and the permeation flux gets temperature dependent in the range of relatively low temperatures (cf. Fig. 2). Membrane annealing during a few minutes at 800°C restored the initial state due to the dissolution of the deposited film in the membrane bulk. At $T_m > 750$°C, ASS deposition with a rate of $\approx 10^{16}$ H

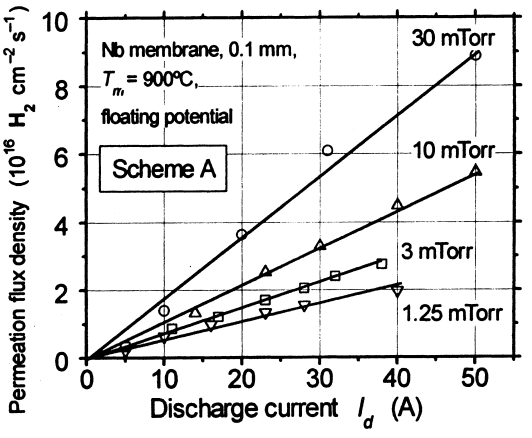

Fig. 3. Dependence of permeation flux density on discharge current at different values of hydrogen pressure at the upstream side (obtained with the Scheme A).

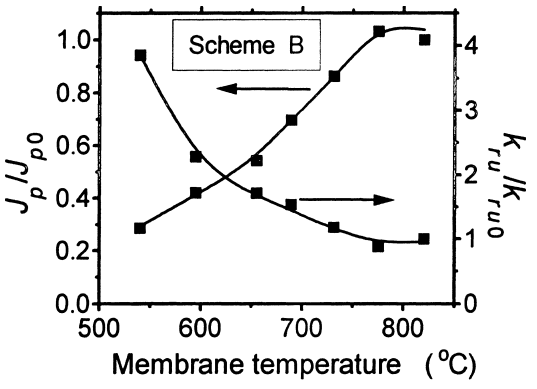

Fig. 4. Temperature dependencies of the effect of ASS deposition on plasma driven permeation flux, j_p, normalized to its initial value, j_{p_0}, and of the recombination rate constant, k_{ru}, normalized to its initial value, k_{ru0}. The doses of ASS deposited at each T_m were $\approx 2 \times 10^{16}$ atom/cm^2 (with the initial state restored by annealing at 800°C at every next T_m). The Nb membrane was at a floating potential, and the ASS target bias was 400 V relative to the plasma.

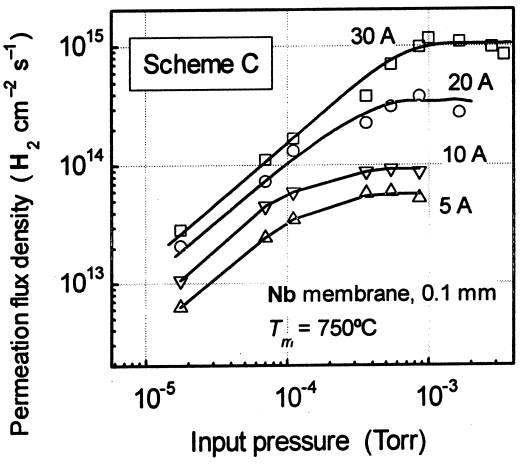

Fig. 5. Dependence of permeation flux on the H_2 pressure around the linear He plasma (Scheme C) at several values of the discharge current in the plasma source, I_d, responsible for plasma density, n_e.

cm^{-2} min^{-1} had no effect on the superpermeable membrane operation (Fig. 4), at least, during the time of observation (in tens of minutes). That occurs due to the fast dissolution of deposited species during deposition.

Permeation of hydrogen neutrals generated by He plasma (*Scheme C*) in a linear plasma device [12]. The dependence of j_p on the pressure, p_{H_2}, of the ambient hydrogen around the He plasma column is presented in Fig. 5 at several values of the discharge current in the plasma source, I_d. At relatively low p_{H_2}, hydrogen does not interfere with the primary He plasma. The rate of generation of energetic hydrogen is proportional to p_{H_2}, and thus j_p must be proportional to p_{H_2}, if the major part of energetic neutrals permeates through the membrane, which is actually observed. At higher H_2 pressures, the electrons of primary He plasma are losing their energy mainly in inelastic collisions with hydrogen, and that is the cause of j_p saturation. Notice that $j_p \propto I_d$ (and thus $j_p \propto n_e$ [12]) is obeyed at all p_{H_2} investigated.

6. Conclusions

A stable plasma driven superpermeation was observed with three different plasma devices on niobium and vanadium membranes of different shape, size and wall thickness. The plasma driven superpermeation demands no special efforts to maintain if the energy of incident hydrogen particles is below 50–70 eV: the sputtering threshold of monolayer nonmetallic (O, C) films. A superpermeation flux density of $\approx 10^{17}$ H cm^{-2} s^{-1} is reached in the plasma membrane experiments. Deposition of the components of austenitic stainless steel (Fe, Cr) on the upstream surface of a Nb membrane may destroy its superpermeability, if the membrane temperature, T_m, is not high enough; an in situ annealing of membrane at $T_m > 750$°C restores its properties. It was found that He plasma containing a small hydrogen impurity may be combined with a superpermeable membrane to effectively isolate hydrogen.

Acknowledgements

This work was partly supported by the Association Euratom-CEA under Contract CEA/V.2910.001 with EURATOM and by a grant no. 98-02-18248 of the Russian Foundation for Basic Research.

References

[1] A.I. Livshits, M.E. Notkin, A.A. Samartsev, J. Nucl. Mater. 170 (1990) 74.
[2] A.I. Livshits, M.E. Notkin, A.A. Samartsev, A.O. Busnyuk, A.Yu. Doroshin, V.I. Pistunovich, J. Nucl. Mater. 196–198 (1992) 159.
[3] A. Livshits, N. Ohyabu, M. Notkin, V. Alimov, H. Suzuki, A. Samartsev, M. Solovyov, I. Grigoriadi, A. Glebovsky, A. Busnyuk, A. Doroshin, K. Komatsu, J. Nucl. Mater. 241–243 (1997) 1203.
[4] A.I. Livshits, M.E. Notkin, V.I. Pistunovich, M. Bacal, A.O. Busnyuk, J. Nucl. Mater. 220–222 (1995) 259.
[5] M. Bacal, F. El Balghiti-Sube, A.I. Livshits, M.E. Notkin, M.N. Solovyev, in: C. Varandas, F. Serra (Eds.), Fusion Technology 1996, Elsevier, Amsterdam, 1997, p. 1157.
[6] J. Park, T. Bennet, J. Schwarzmann, S.A. Cohen, J. Nucl. Mater. 220&222 (1995) 827.
[7] N. Ohyabu et al., J. Nucl. Mater. 220–222 (1995) 298.
[8] M. Bacal, F. El Balghiti-Sube, A.I. Livshits, M.E. Notkin, D. Riz, M.N. Soloviev, T. Kuroda, M.Y. Tanaka, Rev. Sci. Instrum. 69 (1998) 935.
[9] K. Morita, K. Mori, Y. Muto, J. Nucl. Mater. 196–198 (1992) 564.
[10] C. Courteille, A.M. Bruneteau, M. Bacal, Rev. Sci. Instrum. 66 (1995) 2533.
[11] E. Fromm, E. Gebhardt (Eds.), Gase und Kohlenstoff in Metallen, Springer, Berlin, 1976.
[12] N. Ohno et al., J. Nucl. Mater. 220–222 (1995) 279.
[13] A. Livshits, F. Sube, M. Notkin, M. Soloviev, M. Bacal, J. Appl. Phys. 84 (1998) to be published.