ELSEVIER

Journal of Nuclear Materials 307–311 (2002) 1520–1523

journal of nuclear materials

www.elsevier.com/locate/jnucmat

Hydrogen permeation through metal membrane with protective coating in contact with atomic or ionized hydrogen

V.M. Sharapov *

Institute of Physical Chemistry, Russian Academy of Sciences, Leninsky pr., 31, Moscow 119991, Russia

Abstract

The use of protective coatings is one of the most common methods to reduce the hydrogen permeation through structural materials. Considering the hydrogen permeation through such multilayer membrane it is usually suggested that the ratio of hydrogen concentrations at the interface is equal to that of the hydrogen equilibrium solubilities in these materials. However, during diffusion permeation the hydrogen concentrations at the interface are not equilibrium values but they are determined by diffusion input D_1/d_1 and output D_2/d_2 rates and by passage rate through interface which is proportional to the ratio of equilibrium solubilities S_1 and S_2 (d_i, D_i – thickness of and hydrogen diffusivity in i-layer, respectively). Therefore the ratio of hydrogen concentrations at the interface can be adopted by the ratio $(S_1D_1/d_1)/(S_2D_2/d_2)$. By this approximation the analysis of hydrogen permeation through the duplex membrane in a diffusion-limited regime showed that the coating of the same materials can both decrease and increase the hydrogen permeability of the system depending on the ratio of these parameters. In this case it is possible to explain the contradictory results of experiments on hydrogen permeation through duplex membranes.

1. Introduction

The study of interaction of hydrogen isotopes with two-layer systems has a great interest in the frame of fusion reactor problems because such systems may be formed in the tokamak discharge chamber in result of sputtering of different construction elements. It is necessary to take into account the influence of the forming coating of sputtered materials on the hydrogen accumulation, reemission and permeation in/from/through structural materials for the evaluation of hydrogen isotopes balance in the tokamak chamber.

It is well-known that the use of the protective coating is one of the wide-spread methods for reducing of the hydrogen permeability of structural metals. The materials with a hydrogen solubility lower than that in structural metals are usually used as protective coatings in conditions of interaction with *molecular* hydrogen. The low hydrogen solubility of the coating leads to the reduction of hydrogen permeation through the metal.

However, the experimental results on hydrogen permeation through the metals with protective coatings in conditions of interaction with *hydrogen ions or plasma* are contradictory. There is a number of experimental work [1–3] which had shown that the coatings of the same material can both increase and decrease the permeability of structural material in these conditions.

This work is devoted to consideration of hydrogen permeation through metal membranes with coating *in non-equilibrium conditions* in contact with ionized or atomic hydrogen. This consideration does not take into account the isotopic effects and is valid for protium, deuterium and tritium.

---

* Tel.: +7-095 330 0965; fax: +7-095 334 8531.
E-mail address: sharapov@ipc.rssi.ru (V.M. Sharapov).

0022-3115/02/$ - see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0022-3115(02)01300-4

2. Results and discussion

The experiments on deuterium permeation through bare nickel and nickel with a tungsten coating at upstream side of the membrane in contact with molecular deuterium and low energy deuterium plasma (ions and atoms flux = 2.4×10^{16} cm^{-2} s^{-1}, ion energy = 20–350 eV) were performed in the temperature range 700–1000 K [1]. The tungsten coating was deposited on the nickel membrane of a thickness 0.5 mm by a magnetron sputtering method. The thickness of the tungsten film was of 0.05 μm. Tungsten was chosen because (i) tungsten is one of the advanced materials for fusion reactors and (ii) the hydrogen solubility in tungsten is very small (much less than in other structural metals). Nickel is a conventional material for such model experiments.

It was shown firstly that the hydrogen permeation was in the diffusion-limited regime and secondly, the tungsten coating really decreases the deuterium permeability of nickel both in contact with molecular deuterium and with the plasma (Fig. 1), although this decrease is not so significant as it might be expected from the difference of hydrogen solubilities in these metals.

Let us consider the process of hydrogen permeation through a two-layer membrane. In the diffusion-limited regime the steady-state permeating flux P is equal to:

$$P = D_C(c_1 - c_2)/d_C = D_S(c_3 - c_4)/d_S, \tag{1}$$

here D_C, D_S, d_C, d_S – are hydrogen diffusivities in and layer thicknesses of coating and substrate, respectively; c_1 and c_4 – near-surface hydrogen concentrations at upstream (coating) and downstream (substrate) surfaces, respectively; c_2 and c_3 – hydrogen concentrations in coating and substrate at the interface between the two materials.

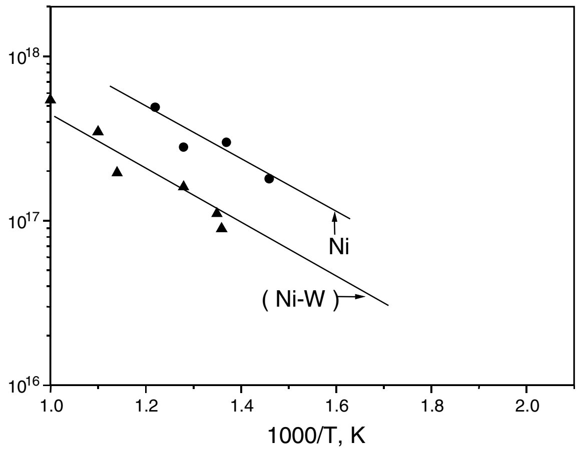

Fig. 1. Temperature dependence of deuterium permeation flux through bare nickel and through nickel with tungsten coating under plasma bombardment; incident flux density 2.4×10^{20} D/m^2 s, ion energy 50 eV.

Usually one suppose that the ratio of hydrogen concentrations at the interface between the two materials c_2 and c_3 is equal to the ratio of hydrogen solubilities in these materials S_C and S_S (see for example, [2,4]). However, it seems that it is not always fulfilled for the permeation process. Equilibrium solubility determines the hydrogen content in the metal at definite temperature and pressure under thermodynamic equilibrium conditions. During the permeation the hydrogen concentration at the interface is not the equilibrium value and it is determined by the ratio of the surface process rate (which is proportional to solubility) and diffusion input D_C/d_C and output D_S/d_S rates. If the passing rate through the interface is small and the diffusion output rate in the substrate is fast then the hydrogen concentration in the substrate at the interface cannot reach the equilibrium value whereas the hydrogen concentration at the interface in the coating can exceed the equilibrium solubility under conditions of ion bombardment. Therefore, let us consider that in the first approximation the ratio of hydrogen concentrations at the interface c_2/c_3 can be adopted to real situation by the ratio:

$$\begin{aligned} c_2/c_3 = M &= (S_C D_C/d_C)/(S_S D_S/d_S) \\ &= (S_C D_C d_S)/(S_S D_S d_C). \end{aligned} \tag{2}$$

Note that the same term appeared in the analyses of the 'time-lag' constant in the description of the nonstationary stage of hydrogen permeation through multilayer membranes [5,6]. Combining expressions (1) and (2) and supposing $c_4 \approx 0$, the expressions for the concentration c_2 and permeating flux P were obtained after simple transformations:

$$c_2 = Mc_3 = MP(d_S/D_S), \tag{3}$$

$$P = c_1(D_C/d_C)(1/[1 + A]), \tag{4}$$

here

$$A = (D_C d_S/D_S d_C)M = (D_C d_S/D_S d_C)^2(S_C/S_S). \tag{5}$$

When the atomic or ionized hydrogen flux Q interacts with the membrane the hydrogen concentration c_1 is connected with the reemitted flux J_R by the expression (for example, [4]):

$$J_R = K_C c_1^2, \tag{6}$$

here K_C is the recombination coefficient in m^4/s.

When the permeating flux P is much less then the incoming flux Q (not superpermeation regime) then $J_R \approx Q$ and the concentration c_1 is equal to:

$$c_1 = (Q/K_C)^{1/2} \tag{7}$$

and the value of the permeating flux (4) may be presented as:

$$P = \left\{(Q/K_C)^{1/2}\right\}(D_C/d_C)(1/[1+A]). \tag{8}$$

Based on the ratio of the values in (8) it is possible to distinguish two limiting cases:

(i) $A \gg 1$ or $(D_C/d_C)^2 S_C \gg (D_S/d_S)^2 S_S$,

i.e. the product of diffusion transfer rate and hydrogen solubility in the coating is higher than that for the substrate.

In this case the steady-state permeating flux P is equal to:

$$\begin{aligned} P &= \left\{(Q/K_C)^{1/2}\right\}(D_S/d_S)^2(d_C/D_C)(S_S/S_C) \\ &= \left\{(Q/K_C)^{1/2}\right\}(D_S^2 d_C S_S/D_C d_S^2 S_C). \end{aligned} \tag{9}$$

(ii) $A \ll 1$ or $(D_C/d_C)^2 S_C \ll (D_S/d_S)^2 S_S$.

In this case the steady-state permeating flux P is equal to:

$$P = \left\{(Q/K_C)^{1/2}\right\}(D_C/d_C). \tag{10}$$

i.e. it is entirely determined by the recombination coefficient and the diffusivities of hydrogen in the coating.

In order to analyse the influence of the coating on hydrogen permeation through a two-layer membrane let us compare the permeability of membranes with coating and without coating. The permeability of a one-layer membrane in the diffusion-limited regime is equal to:

$$P_S = \left\{(Q/K_S)^{1/2}\right\}(D_S/d_S). \tag{11}$$

The ratio of the permeability of the membrane with coating to that without coating in case (i) is equal to:

$$P/P_S = \left\{(K_S/K_C)^{1/2}\right\}(D_S d_C S_S/D_C d_S S_C) \tag{12}$$

and in case (ii):

$$P/P_S = \left\{(K_S/K_C)^{1/2}\right\}(D_C d_S/D_S d_C). \tag{13}$$

Let us analyse the experimental results which were described above taking into account the kinetic factors for the hydrogen concentrations at the interface between tungsten and nickel. The calculations were done at 723 K because the analogous experiments were fulfilled at the same temperature [2] which will be discussed later.

The hydrogen diffusivity $D_W = 6 \times 10^{-10}$ m^2/s and solubility $S_W = 4.8 \times 10^{16}$ at/m^3 Pa$^{1/2}$ in tungsten were calculated on the base of data in [7], the recombination rate of hydrogen on the tungsten surface $K_W = 2 \times 10^{-21}$ m^4/s was obtained in [1]. The parameters of the interaction of hydrogen with nickel were calculated on the base of data in [8,9]:

$$D_{Ni} = 8.6 \times 10^{-10}\ \text{m}^2/\text{s};$$

$$S_{Ni} = 7.8 \times 10^{22}\ \text{at/m}^3\,\text{Pa}^{1/2}; \quad K_{Ni} = 4.6 \times 10^{-27}\ \text{m}^4/\text{s}.$$

Using these values the parameter A was calculated which proved to be 30, i.e. $A \gg 1$. Therefore expression (12) was used for the calculation of the deuterium permeability. After calculation, $P_{W+Ni}/P_{Ni} = 0.3$ was obtained, i.e. the permeability of the nickel membrane with tungsten coating was proved by a factor approximately 3 lower than that of bare nickel. It is practically the same obtained experimentally (decreasing 2.5 times).

However, Anderl et al. [2] showed experimentally that the deuterium permeability of a copper membrane of a thickness 0.5 mm with tungsten coating of 0.5 μm at 723 K is one order of magnitude higher than that of a bare copper membrane of the same thickness in conditions of 3 keV D_3^+-ion bombardment.

These authors investigated also the deuterium permeation through the membrane of stainless steel 316 with tungsten coating in conditions of the same irradiation [3]. When the tungsten coating of 1 μm thickness was produced using the sputter-deposition technique, the deuterium permeation rate through the composite sample was higher than that through bare SS 316 membrane of the same thickness 0.5 mm at 770 K. However, the deuterium permeation through the stainless steel membrane with plasma-sprayed tungsten coating (the coating and substrate thicknesses were 0.021 and 0.564 mm, respectively) was by a factor of 10^3 and 10^4, respectively below those through the bare steel and the sputter-deposited tungsten/steel specimens (Fig. 2).

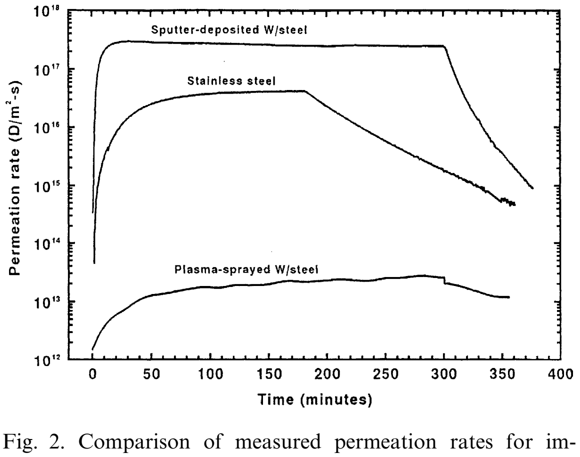

Fig. 2. Comparison of measured permeation rates for implanted deuterium in speciments at 770 K [3].

These results do not seem surprising if the kinetic factor is taken into account. Really, it follows from the expressions (12) and (13) that the ratio of P/P_S can be both higher and lower than unity depending on the ratio of parameters which are included in these expressions. It means that the coating of the same materials can both increase or decrease the permeability of metals.

Let us consider the system tungsten–copper. As mentioned above Anderl et al. showed that the tungsten coating increases the deuterium permeability of the copper membrane by one order of magnitude. They pointed out in the discussion that they expected to obtain an increase of P approximately two hundreds times more as it follows from a model in which it is suggested that the ratio of deuterium concentrations in copper and in tungsten at the interface is equal to the ratio of equilibrium solubilities of deuterium in these metals.

Let us do the same calculations as previously to describe the deuterium permeation through this system. The interaction parameters of hydrogen with tungsten and copper were used from [2] (the hydrogen solubility in tungsten was calculated on the base of data in [7]):

$$D_W = 6 \times 10^{-10}\ \mathrm{m^2/s}; \quad S_W = 4.8 \times 10^{16}\ \mathrm{at/m^3\,Pa^{1/2}};$$
$$K_W = 1 \times 10^{-22}\ \mathrm{m^4/s};$$
$$D_{Cu} = 1 \times 10^{-9}\ \mathrm{m^2/s}; \quad S_{Cu} = 1.1 \times 10^{21}\ \mathrm{at/m^3\,Pa^{1/2}};$$
$$K_{Cu} = 3 \times 10^{-24}\ \mathrm{m^4/s}.$$

The value of the parameter A was proved to be 15.5, i.e. $A \gg 1$ and the same expression (12) was used for the evaluation of the coating influence. A simple calculation obtained $P_{W+Cu}/P_{Cu} = 4.7$. Thus, the deuterium permeability of the two-layer system tungsten–copper proved to be higher by a factor of almost 5 than that of the bare copper membrane of the same thickness. This conclusion correlates quite well with experimental results in [2].

3. Conclusions

The considerations of hydrogen permeation through a two-layer membrane in the diffusion-limited regime was carried out taking into account kinetic factors in the determination of hydrogen concentrations at the interface of two metals. It was shown that in this case it is possible to explain that the coating of the same materials can both increase and decrease the permeability of metal.

This approach was used for describing the hydrogen permeation through the systems tungsten–nickel and tungsten–copper. The results obtained are close to the experimental ones.

The expressions obtained can be used both for the evaluation of the efficiency of the given protective coating and for the evaluation of the coating thickness for changing the hydrogen permeability of structural materials.

Acknowledgement

The author is grateful to Professor A. Zakharov for the assistance and useful discussion.

References

[1] V.M. Sharapov, L.E. Gavrilov, Gas- and plasma – driven deuterium permeation through duplex membrane tungsten – nickel, Book of abstracts of 14th International Conference on Plasma Surface Interactions in Controlled Fusion Devices, Rosenheim, Germany, 22–26 May 2000, P-2.23; V.M. Sharapov, L.E. Gavrilov, Russian Journal of Physical Chemistry 75 (2001) 2079.

[2] R.A. Anderl, D.F. Holland, G.R. Longhurst, J. Nucl. Mater. 176&177 (1990) 683.

[3] R.A. Anderl, R.J. Pawelko, M.R. Hankins, G.R. Longhurst, R.A. Neiser, J. Nucl. Mater. 212–215 (1994) 1416.

[4] F. Waelbroeck, Influence of bulk and surface phenomena on the hydrogen permeation through metals, Berichte der Kernforschungsanlage Jülich, Jül-1966, 1984.

[5] H. Züchner, Proc. JIMIS-2: Hydrogen in Metals 101 (1977).

[6] T.N. Kompaniets, A.A. Kurdyumov, Prog. Surf. Sci. 17 (1984) 75.

[7] R.J. Frauenfelder, J. Vac. Sci. Technol. 6 (1969) 388.

[8] K.L. Wilson, R. Bastasz, R.A. Causey, et al., Suppl. J. Nucl. Fusion 1 (1991) 31.

[9] B.L. Doyle, D.K. Brice, Radiat. Eff. 89 (1985) 21.