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RADIATION-INDUCED DRIFT OF HYDROGEN AND ITS TRAPPING IN METALLIC MEMBRANES AND PARTICLES

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On the basis of a multistage approach to the description of the absorption of hydrogen in metals, some questions concerning the radiation-induced mass transfer of hydrogen, as well as its trapping in metallic membranes and aerosol particles, are considered.

At the present time, the attention of researchers is being turned increasingly to questions connected with different aspects of the processes of transfer and absorption of hydrogen. First of all, this is connected with efforts to implement the ideas of hydrogen energetics [1]. One of the problems of highest current interest in this field is storage of hydrogen. In turn, this question is connected with an investigation of the processes of hydrogen transfer in various systems. The present work deals with the influence of heterogeneous processes on initiation of mass transfer of hydrogen in metallic membranes with the aid of excitation of hydrogen molecules (for example, on exposure to laser radiation) as well as on trapping (absorption) of hydrogen by metallic membranes (films) and aerosol particles.

It is known that dissolution of hydrogen in metals is usually an activated process through overcoming several potential barriers [2–4]. On collision of a hydrogen molecule with the metal surface, both reflection of the molecule back to a gas phase and dissociative chemisorption (formation of hydrogen atoms with their subsequent chemisorption) may occur, the realization of which necessitates overcoming a certain potential barrier. The next stage turns out to be the passage of chemisorbed atoms into the metal lattice, which is also related to overcoming a potential barrier. The exit of hydrogen from the metal is due to overcoming potential barriers in the passage of a dissolved (absorbed) hydrogen atom onto the metal surface and subsequent recombination of atoms and desorption of the resultant hydrogen molecules. The scheme of penetration of hydrogen into the metal and its emergence from it is presented in Fig. 1.

Coating of the metal surface by a thin layer of a particular substance can essentially change the course of the processes occurring on the surface, which, in turn, leads to the appearance of new effects, in particular, to an appreciable rise in the permeability of the metallic membrane to high-energy particles [5, 6]. Such coatings can consist of nonmetallic films, for example, films of oxygen, carbon, and sulfur deposited specially onto the metal surface or produced naturally [6]. In [7], it is shown that deposition of a thin layer of Al_2O_3 on the surface of an MgAl film can raise the content of hydrogen in the film. The effects mentioned are related to the fact that hydrogen atoms having sufficiently high energy penetrate through the layer of the substance deposited on the membrane into the crystal lattice of the metal where they are "cooled" coming to equilibrium with the lattice [6]. However, egress of hydrogen from the metal is hindered by a sufficiently high potential barrier (which can be made higher as a result of the coating of the surface by a specific substance) for the processes of passage of hydrogen atoms onto the surface of the system and their recombination with the formation of molecules. Alternation of the probability of dissociation of a hydrogen molecule incident on the surface (which can be connected with excitation of the molecule) also influences the mass transfer of hydrogen in the membrane.

Below, we consider some questions connected with the initiation of mass transfer in metallic membranes on excitation of hydrogen molecules in a gas phase; this leads to a decrease in the potential barrier for dissociative chemisorption of excited (for example, by laser radiation [8] or electron shock [9]) hydrogen molecules, as well as problems

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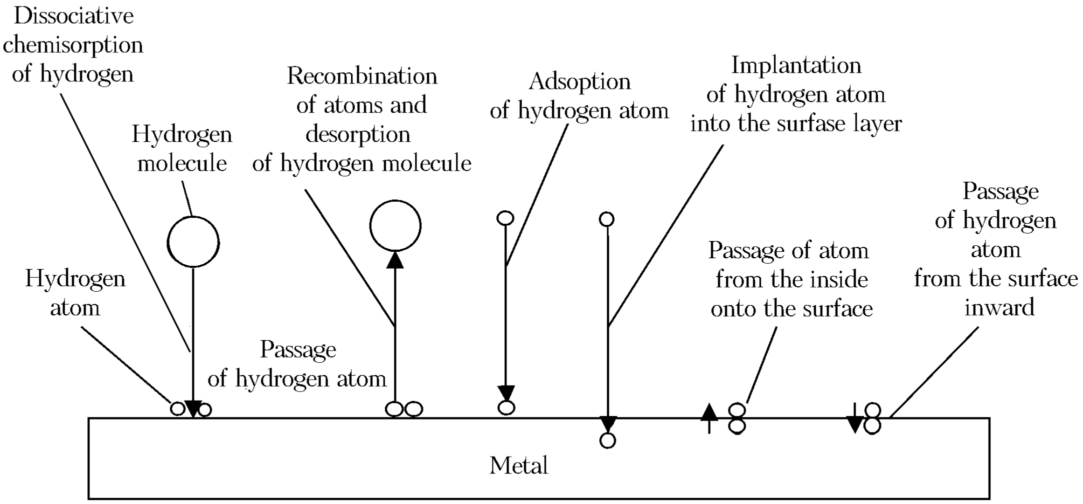

Fig. 1. Geometric scheme of the hydrogen–metal interaction.

of the capacity of metallic membranes and spherical particles relative to hydrogen. We note that some of the problems of the radiation-induced drift of gas molecules in capillaries and membranes are treated in [10–12].

Hereafter, in investigating transfer processes in the hydrogen–metal system assumed to be isothermal, we consider that dissociative chemisorption is realized on direct collision of a hydrogen molecule with a surface [13], whereas the possibility of the hydrogen molecule being in the state of physical adsorption is not considered, just as in [3] (the model taking account of physical adsorption of hydrogen molecules on the surface was discussed in [14]). We also ignore the processes of direct transition of hydrogen atoms formed in the process of dissociation of its molecules in the gas phase into the surface layer of the membrane (without intermediate residence in the state of chemisorption) and the inverse process of direct passage of atoms from the surface layer into the gas phase (with recombination into molecules) without residence in the state of chemisorption. Moreover, we do not take into consideration the emergence of hydrogen in the form of atoms from the membrane into the gas phase. The concentrations of hydrogen atoms both in the adsorbed layer and in the bulk phase are considered to be sufficiently low, so that the phenomena of blocking atomic transitions from one position to another by the hydrogen atoms present in the given phase can be neglected.

Taking into consideration the above assumptions for the flux densities of the molecules dissociating on the surface of the membrane (I_1) and of those formed on recombination of the hydrogen atoms present on the surface (I_2), as well as for the flux densities of the hydrogen atoms that pass from the state of chemical adsorption into the surface layer of the membrane (I_3) and from the latter into the state of chemical adsorption (I_4), and following [3] we can write the expressions

$$I_1 = k_1 J\,, \quad I_2 = k_2 n^2\,, \quad I_3 = k_3 n\,, \quad I_4 = k_4 c\,. \tag{1}$$

Here k_i (i = 1–4) are the rate constants of respective processes which are exponentially dependent on the activation energies of these processes and temperature:

$$k_i = k_i' \exp\left\{-\frac{Q_i}{kT}\right\}, \tag{2}$$

where k_i' are preexponential factors assumed to be constant values; Q_i are the effective activation energies of respective processes [3]. It should be noted that k_1 is the sticking coefficient for the process of chemisorption of a hydrogen molecule [4]. The value of the flux density of the hydrogen molecules incident on the membrane surface, under the assumption of the Maxwellian velocity distribution function of molecules, takes the form

$$J = \frac{P}{(2\pi mkT)^{1/2}}\,. \tag{3}$$

If there are hydrogen atoms in the gas phase, their direct chemisorption on the membrane surface can occur, as well as implantation of atoms directly into the membrane volume [6]. Here, the following relation can be written:

$$\varphi = 1 - \beta - \gamma , \tag{4}$$

where φ and β are respectively the coefficient (probability) of elastic reflection of an atom from the membrane surface and the coefficient of sticking of an atom to it; γ is the coefficient of implantation of hydrogen atoms, which characterizes the probability that the atom impinging on the membrane would enter directly into its volume.

For the concentration of hydrogen atoms in the membrane the following equation can generally be written (next we assume that only hydrogen atoms can be implanted into the membrane):

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial X}\left(D \frac{\partial c}{\partial X} \right) + J_{a0} F_0 (X) + J_{aL} F_L (X) + q^+ - q^- , \tag{5}$$

where q^+ is the volume source of hydrogen atoms appearing in the membrane, in particular, when they emerge from the cavities (bubbles) that can be present in it [7], and pass into the crystal lattice; q^- is the sink of hydrogen atoms (for example, into the cavities mentioned) in a unit volume in unit time; the difference in the functions $F_0(X)$ and $F_L(X)$ for the opposite sides of the membrane can be due to different properties of the surface layers at $X = 0$ and $X = L$. Here gaseous hydrogen is present in the cavities as molecules [7] and its transfer from the cavities into the crystal lattice and back should be described by expressions of type of (1).

The initial and boundary conditions for Eq. (5) can be represented as

$$c \big|_{t=0} = 0 , \tag{6}$$

$$- D \frac{\partial c}{\partial X}\bigg|_{X=0} = k_{30} n_0 - k_{40} c (0) , \tag{7}$$

$$- D \frac{\partial c}{\partial X}\bigg|_{X=L} = k_{4L} c (L) - k_{3L} n_L . \tag{8}$$

Here n_0 and n_L are determined by the expressions

$$\frac{dn_0}{dt} = 2k_{10} J_0 - 2k_{20} n_0^2 + k_{40} c (0) - k_{30} n_0 + \beta J_{a0} , \tag{9}$$

$$\frac{dn_L}{dt} = 2k_{1L} J_L - 2k_{2L} n_L^2 + k_{4L} c (L) - k_{3L} n_L + \beta J_{aL} , \tag{10}$$

$$n_0 \big|_{t=0} = 0 , \tag{11}$$

$$n_L \big|_{t=0} = 0 , \tag{12}$$

where J_0, k_{10}, k_{20}, k_{30}, k_{40}, n_0 and J_L, k_{1L}, k_{2L}, k_{3L}, k_{4L}, n_L are the values of corresponding quantities at $X = 0$ and $X = L$.

We consider the induced mass transfer of hydrogen in a metallic membrane on excitation of its molecules (for example, by laser radiation [8]) near one of the sides of the membrane (for the sake of definiteness, we assume that the molecules are excited at $X = 0$). In this case we reason, for simplicity, that only molecular hydrogen is present in the gas phase, and the terms in (5), (9), and (10) involving the flux density of atomic hydrogen can be neglected. We also assume that the sources and sinks of hydrogen are absent in the membrane ($q^+ = q^- = 0$) and the pressure of molecular hydrogen is the same on both sides of the membrane ($P_0 = P_L = P$).

Further, to simplify the analysis, we apply the approach used in [15]. We introduce the effective rate constants of direct and inverse processes of the entry of molecules into the membrane (k_0^+, k_L^+) and their exit from it (k_0^-, k_L^-) at $X = 0$ and $X = L$, respectively. In this case, the boundary conditions for the diffusion equation are written as

$$-D\left.\frac{\partial c}{\partial X}\right|_{X=0} = k_0^+ P - k_0^- c\,(0)\,, \tag{13}$$

$$-D\left.\frac{\partial c}{\partial X}\right|_{X=L} = k_L^- c\,(L) - k_L^+ P\,, \tag{14}$$

where the quantities k_0^+, k_0^-, k_L^+, and k_L^-, based on [3, 15], can be presented as

$$k_0^+ = \frac{2\alpha_0 k_{30}}{k_{30} + 2k_{20}n_0}\,,\quad k_L^+ = \frac{2\alpha_L k_{3L}}{k_{3L} + 2k_{2L}n_L}\,,\quad k_0^- = \frac{2k_{40}k_{20}n_0}{k_{30} + 2k_{20}n_0}\,,\quad k_L^- = \frac{2k_{4L}k_{2L}n_L}{k_{3L} + 2k_{2L}n_L}\,. \tag{15}$$

Here, $\alpha_0 = \dfrac{k_{10}}{(2\pi mkT)^{1/2}}$, $\alpha_L = \dfrac{k_{1L}}{(2\pi mkT)^{1/2}}$, and the factor in (15), which is equal to 2, appears due to the conversion of the flux density of hydrogen molecules into the flux density of atoms.

We note that in [5] boundary conditions of the type of Eqs. (13) and (14) are used with the effective coefficients which, respectively, are determined as the probability of adsorption of a gas particle after one impact on the surface and the probability of the exit of the particle present in the membrane into the gas phase, when it arrives once at the inner surface of the membrane. Further, just as in [15], we shall consider for simplicity that the values of k_0^+, k_0^-, k_L^+, and k_L^- are independent of the concentration of adsorbed molecules n. In so doing, in a first approximation we assume that $n_0 = n_L = \bar{n} = n_{\text{eq}}$, where n_{eq} is the concentration of chemisorbed hydrogen atoms on the surface of the membrane at equilibrium, when the resulting flux of hydrogen through the membrane is equal to zero.

We consider the situation in which the laser radiation that excites hydrogen molecules is directed parallel to the surface of the membrane (at $X = 0$) and acts only on the molecules present in the gas phase. At the same time, the influence of radiation on the membrane surface and the hydrogen atoms adsorbed on it will be neglected. For simplicity, a two-level model of excitation of molecules is used. Here, we do not consider the possibility of dissociation of an excited molecule into atoms in the gas phase. The question of the presence of hydrogen atoms in the gas and their implantation into the solid phase will be considered below. In the case of excitation of hydrogen molecules, the dissociation energy of an excited molecule decreases, which accordingly results in a change in the values of k_{10}, α_0, and k_0^+. In what follows, we assume that $k_{20} = k_{2L} = k_2$, $k_{30} = k_{3L} = k_3$, and $k_{40} = k_{4L} = k_4$. Satisfaction of these conditions leads to the equality $k_0^- = k_L^- = k^-$.

In view of the above assumptions, the value of α_0^* corresponding to the case where a part of hydrogen molecules is in an excited state is determined by the expression

$$\alpha_0^* = \frac{k_{10}^*\nu}{(2\pi mkT)^{1/2}} + \frac{k_{10}\,(1-\nu)}{(2\pi mkT)^{1/2}}\,. \tag{16}$$

Here the parameter ν represents the fraction of hydrogen molecules in the excited state and it is found from the kinetic equations for transition of molecules from the ground state to the excited one and back; k_{10}^* is the rate constant of dissociative chemisorption for an excited molecule, which can be represented as

$$k_{10}^* = k_1'\exp\left(-\frac{2E_{\text{c}} - \Delta Q_{\text{v}}}{kT}\right), \tag{17}$$

where E_c is the activation energy of chemisorption [3, 4] and ΔQ_ν characterizes the change in the activation energy of dissociative chemisorption in the case of excitation of a hydrogen molecule.

The solution of the steady-state diffusion equation for hydrogen atoms in the membrane taking into account the foregoing and the assumption that the quantities J_{a0}, J_{aL}, q^+, and q^- are equal to zero leads to the following relation for the density N of the net flux of hydrogen molecules passing through the membrane:

$$N = \frac{\nu\,(k_{10}^* - k_{10})\,P}{(2\pi mkT)^{1/2}} \frac{k_3}{k_3 + 2k_2\bar{n}} \left(2 + \frac{k^- L}{D} \right)^{-1} . \tag{18}$$

As follows from (18), on satisfaction of the inequality

$$\frac{k^- L}{D} << 1 \tag{19}$$

the quantity N is independent of the diffusion coefficient and parameters of the membrane but is determined only by the surface processes (condition (19) corresponds to multiple reflections of a hydrogen atom from the inner surfaces of the membrane until its exit from the latter [5], as a result of which a uniform distribution of hydrogen concentration is established in the membrane).

When the pressures of hydrogen on either side of the membrane are equal and excited hydrogen molecules are absent, $\nu = 0$ and the net flux of hydrogen through the membrane is equal to zero. Excitation of hydrogen molecules involves an increase in α_0 and, correspondingly, a rise in k_0^+, which leads to the appearance of the net flux of hydrogen in the membrane. This flux leads, in turn, to an uncompensated impulse on desorption of molecules from the opposite sides of the membrane and accordingly to the resultant force acting on it. It should be noted that in the case of nonequilibrium desorption when there is recombination of atoms on the surface and desorption of the molecules formed takes place, the scattering of molecules, which does not correspond to the cosine law (i.e., the angular distribution of the desorbing molecules is not proportional to cos θ), is of frequent occurrence. The outflowing molecules have a scattering pattern extended along the normal to the surface when the angular distribution of desorbing molecules is proportional to $\cos^\mu \theta$, where $\mu > 1$ [16]. Here, in view of [17], the recoil pressure P' of the hydrogen molecules desorbing from the surface can be estimated as

$$P' = \frac{\mu + 1}{\mu + 2} m v_\mu J_\mu , \tag{20}$$

where J_μ and v_μ are respectively the flux density and the mean velocity of hydrogen molecules desorbing on condition that $\mu > 1$. When the net flux of hydrogen through the membrane differs from zero, the values of J_μ and correspondingly of P' for the opposite sides of the membrane are different.

As follows from (18) and (20), excitation of hydrogen molecules near one of the surfaces of the metallic membrane can lead both to the appearance of the net flux of hydrogen passing through the membrane and to the appearance of a difference in the recoil pressures of the molecules desorbing from the opposite sides of the membrane and, correspondingly, to the initiation of the net force acting on it. Here, on satisfaction of condition (19), it is the processes on the interface that turn out to be limiting ones [5, 6, 7, 18]. If excitation of hydrogen molecules occurs in a gas phase near both sides of the membrane, the concentration of hydrogen atoms in it will increase due to the aforesaid. The same applies to a metallic aerosol particle.

The phenomena considered above can be more intense when on exposure of hydrogen molecules to external influences, along with excitation of molecules, their dissociation into atoms in a gas phase occurs, and both excited molecules and hydrogen atoms fall on the membrane surface. These phenomena can also take place when the surface of the membrane is covered by a coating which hampers the exit of hydrogen from the surface. The phenomena mentioned are responsible for the superpermeability of metallic membranes [5, 6], and they lead to an increase in the amount of hydrogen in such a membrane (film) [7]. The noted trends in the transfer and trapping of hydrogen in membranes can be used in the processes of its extraction from gas mixtures.

We shall analyze the question concerning the absorptivity of a metallic membrane relative to hydrogen in the presence of a stream of hydrogen atoms being implanted into it. The possibility of such an implantation is connected with the sufficiently high energy of hydrogen atoms [6, 19]. We consider a stationary state of the gas–membrane system with symmetrical conditions on each side of the membrane ($J_0 = J_L = J$, $J_{a0} = J_{aL} = J$, $n_0 = n_L$, $c(0) = c(L) = c$) at $q^+ = q^- = 0$. Based on [3, 4], we can write the following balance relations for determining the concentrations of hydrogen atoms both in the membrane (c) and chemisorbed on its surfaces (n):

$$k_3 n - k_4 c + \gamma J_a = 0 , \tag{21}$$

$$2k_1 J - 2k_2 n^2 + k_4 c - k_3 n + \beta J_a = 0 . \tag{22}$$

From (21) and (22) we have

$$n = \left(\frac{2k_1 J + \chi J_a}{2k_2} \right)^{1/2} , \tag{23}$$

$$c = \frac{k_3}{k_4} \left(\frac{2k_1 J + \chi J_a}{2k_2} \right)^{1/2} + \frac{\gamma}{k_4} J_a , \tag{24}$$

where $\chi = \gamma + \beta$.

At $J_a = 0$ expression (24) subject to (3) is put in a form of the equation of Sieverts [2, 3]. It is seen from (23) and (24) that at $J_a > 0$ the value of c can be substantially higher than in the absence of hydrogen atoms in the gas phase.

Hydrogen can also be trapped by metallic aerosol particles. It should be noted that trapping of molecules and atoms by particles attracts the attention of researchers who deal with both the physicochemical phenomena in the atmosphere (in particular, from the point of view of cleaning it of molecules and atoms of toxic substances) and the processes occurring in contemporary technology, for example, in producing nanoparticles of high purity or of specific composition (alloyed by a specific component). Some questions concerning trapping of admixture component in the course of condensation growth of aerosol particles, as well as during chemical deposition, are considered in [20, 21]. It is shown that in the condensation of an easily condensable substance (for example, of steam), the molecules of the noncondensable component will be trapped by the growing particle. This phenomenon is analogous to cryotrapping, which is widely used in cryogenic technology for pumping almost noncondensable gases.

The regularities connected with the above-considered mass transfer of hydrogen in a plane-parallel metallic membrane are exhibited also in the trapping (absorption) of hydrogen by metallic particles (in particular, with a passivated surface that raises the potential barrier for the process of exit of hydrogen atoms on the surface and their recombination on it). Excitation of hydrogen molecules in a gas phase, which reduces the activation energy for the chemisorption process, leads to an increase in the hydrogen concentration in the particle. As noted above, when high-energy hydrogen atoms are present in a gas phase, their implantation directly into a bulk phase on collision with the particle is possible, which also raises the concentration of hydrogen in the latter. Moreover, similarly to the above-considered case of the membrane, the exit of hydrogen from the particle can be hampered due to sufficiently high potential barriers for the exit of atoms onto the particle surface and their recombination (with subsequent escape of molecules into a gas phase). The regularities mentioned and the fairly large total area of the surface of the particles make it possible to use metallic particles (including nanosized ones) for storage of hydrogen.

For the concentration of hydrogen atoms in a spherical aerosol particle at $q^+ = q^- = 0$ we have the equation

$$\frac{\partial c}{\partial t} = \frac{D}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c}{\partial r} \right) + J_a F(r) . \tag{25}$$

The initial and boundary conditions for the process of particle filling by hydrogen (the stage of "charging") can be written as

$$c\,\big|_{t=0} = 0\,, \tag{26}$$

$$D\left.\frac{\partial c}{\partial r}\right|_{r=R} = k_3 n - k_4 c\,(R)\,, \tag{27}$$

$$\left.\frac{\partial c}{\partial r}\right|_{r=0} = 0\,, \tag{28}$$

where $c(R)$ is the density of hydrogen atoms in the surface layer of the particle (at $r = R$) and n is determined from the equation

$$\frac{dn}{dt} = 2k_1 J - 2k_2 n^2 + k_4 c\,(R) - k_3 n + \beta J_{\text{a}} \tag{29}$$

under the initial condition

$$n\,\big|_{t=0} = 0\,. \tag{30}$$

The quantity of hydrogen atoms in the bulk phase of the particle (G_1) and on its surface (G_2) is found as

$$G_1\,(t) = \frac{4}{3}\,\pi \int_0^R r^3 c\,(t, r)\,dr\,, \tag{31}$$

$$G_2\,(t) = 4\pi R^2 n\,(t)\,. \tag{32}$$

In the steady state, when multiple reflections of hydrogen atoms from the inner surface of the particle occur (until they leave it), which result in a uniform distribution of these atoms inside the particle, for the total amount of hydrogen ($G = G_1 + G_2$) both inside the particle and on its surface in the chemisorbed state, taking account of (23), (24), (31), and (32), we have

$$G = \frac{4}{3}\,\pi R^3 \left\{ \left[\frac{k_3}{k_4} \left(\frac{2k_1 J + \chi J_{\text{a}}}{2k_2} \right)^{1/2} + \frac{\gamma}{k_4}\,J_{\text{a}} \right] + \frac{3}{R} \left(\frac{2k_1 J + \chi J_{\text{a}}}{2k_2} \right)^{1/2} \right\}. \tag{33}$$

It is seen from (33) that the contribution of chemisorbed hydrogen atoms to the total amount of hydrogen in the particle increases with decreasing radius of the latter.

The use of metallic particles of small size for trapping hydrogen leads to an increase in the area of the hydrogen–metal contact surface, which accelerates the process of trapping (absorption) of hydrogen. For example, at a specified mass of material M, the total area of the surface of spherical particles of the same size S_{p} will increase with decreasing radius of the particles: $S_{\text{p}} = 3M/(\rho R)$. However, it should be noted that for nanosized particles the rate constants k_i depend, in principle, on the particle size, which is analogous to the dimensional dependence of the sticking (condensation) coefficient in the processes of physical deposition of gas molecules on small aerosol particles [22]. This leads also to the dependence of the amount of hydrogen in the particles on their size. For example, in [23] data are presented on the capacity of palladium nanoparticles relative to hydrogen, and it is shown that the capacity diminishes with decreasing size of the particle in the range of particle diameters from 4.2 to 0.52 nm. Thus, in this case two factors acting in opposite directions should be allowed for. The smaller the diameter of particles, the larger the area of

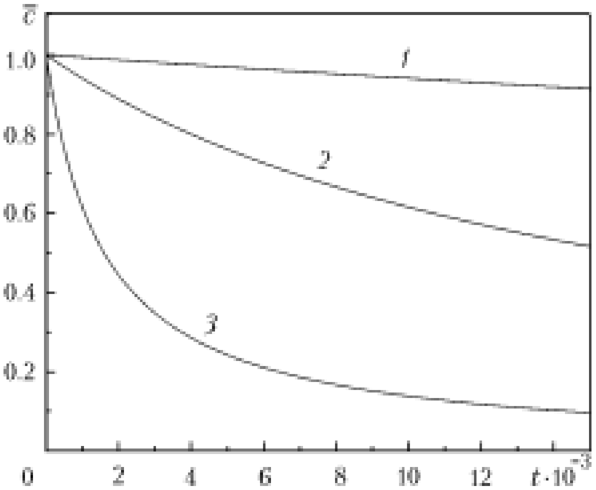

Fig. 2. Time dependence of the relative concentration of hydrogen atoms in a particle $\bar{c}$ at $K_r = 10^{-27}$ cm^4·sec^{-1}, $c' = 10^{17}$ cm^{-3} and different values of the particle radius: 1) $R = 10^{-4}$; 2) 10^{-5}; 3) 10^{-6} cm. t, sec.

their total surface at the specified total mass of material, but the lower the capacity of an individual particle relative to hydrogen.

If a particle containing hydrogen is placed into an atmosphere, where hydrogen is absent, the exit of hydrogen from the particle into the outside atmosphere begins (the stage of "charging"). This phenomenon is of interest in connection with the problem of hydrogen storage. Under the stipulated assumptions in the case, where hydrogen distribution inside the particle can be considered as uniform, in a quasi-stationary approximation the change in the concentration of hydrogen atoms in the particle is written as

$$\frac{R}{3}\frac{dc}{dt} = -2K_r c^2 , \tag{34}$$

where K_r is the effective recombination coefficient, which is usually used for calculating the flux density of the hydrogen molecules outgoing into a gas phase and which is expressed in terms of the volume concentration of hydrogen atoms in the metal. This coefficient can be defined through the constants of elementary processes k_i [3]. The initial condition for Eq. (34), subject to (24), can be written as

$$c\,(0) = c\,' = \frac{k_3}{k_4}\left(\frac{2k_1 J + \chi J_a}{2k_2}\right)^{1/2} + \frac{\gamma}{k_4} J_a , \tag{35}$$

where c' is the concentration of hydrogen atoms in a particle in the steady state in an atmosphere that contains hydrogen molecules and atoms. The solution of Eq. (34) under the initial condition (35) has the form

$$c\,(t) = \frac{c\,'}{\frac{t}{\tau} + 1} , \tag{36}$$

where $\tau = \dfrac{R}{6c'K_r}$.

The recombination coefficient of hydrogen atoms K_r on the surfaces of various metals can be calculated analogously to [3]. For example, in accordance with the computations presented in [3], for niobium at $E_c = 0.2$ eV in the temperature range 500–330 K the value of K_r changes from 10^{-27} to 10^{-32} cm^4·sec^{-1}, respectively (i.e., by five orders). As follows from (36), the concentration of hydrogen atoms in a particle is halved in a time $t' = \tau$. At K_r =

10^{-27} $cm^4 \cdot sec^{-1}$, $R = 10^{-6}$ cm, and $c' = 10^{17}$ cm^{-3} the value of t' is equal approximately to $1.6 \cdot 10^3$ sec (0.44 h). The value of t' diminishes with decreasing radius of the particle and increasing K_r and c'. Figure 2 shows the time dependence of the relative concentration of hydrogen atoms in a particle $\bar{c} = c/c'$ for particles of different sizes. We note that the same dependences $\bar{c}(t)$ (which are characterized by curves 1–3 in Fig. 2) depict the case of $R = 10^{-6}$ cm and $c' = 10^{17}$ cm^{-3} at values of K_r equal to 10^{-29}, 10^{-28}, and 10^{-27} $cm^4 \cdot sec^{-1}$, respectively. Thus, a decrease in the recombination constant K_r (which can be connected, in particular, with the coating of the surface of the particles by different substances or with a decrease in their temperature) leads to a deceleration of the process of hydrogen exit from a particle. For example, for niobium at the above-mentioned parameters a decrease in the temperature from 500 to 330 K results in an increase in t' by approximately five orders. Thus, the stage of hydrogen storage in metallic particles should be realized at sufficiently low temperatures, and, when release of hydrogen from the particles is needed, their temperature must be raised.

In recent years the use of nanosized metallic particles for storing hydrogen has attracted the growing attention of researchers [23, 24]. By now, a number of methods of obtaining both single-component nanoparticles and particles of compound composition (including nanoparticles covered with layers of different substances) have been developed [25]. In the general case, where the exit of hydrogen from a particle is controlled by both the surface processes and diffusion of hydrogen atoms in the particle, and approximation of the uniformity of the concentration of hydrogen in the particle does not hold, for calculating the decrease in its concentration with time (the stage of "discharging") it is necessary to solve the nonstationary diffusion equation (25). Moreover, corresponding initial and boundary conditions should be used, and the interrelation between the concentrations of hydrogen atoms in the surface layer and chemisorbed atoms on the particle surface should be taken into account.

Thus, in this work, on the basis of the concept of the multistage character of the process of hydrogen penetration into metallic membranes and aerosol particles and its exit from these systems, such phenomena as initiation of mass transfer of hydrogen in a membrane on excitation of its molecules in a gas phase, as well as trapping of hydrogen in metallic membranes and aerosol particles have been analyzed. We have discussed the influence of the above-mentioned processes on the size effect when the latter is connected both with an increase in the total area of the surface of particles on decrease in their radius (for the same total mass of the substance) and with a reduction in the capacity of the particles to hydrogen as their size decreases.

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NOTATION

c, concentration of hydrogen atoms in a membrane; *D*, diffusion coefficient of hydrogen atoms in a membrane; $F(X)$ and $F(r)$, functions characterizing distribution of implanted hydrogen atoms over the depth of their penetration into a membrane or a particle; J and J_a, flux densities of hydrogen molecules and atoms incident on the surface of a membrane; K_r, effective recombination coefficient; *k*, Boltzmann constant; *L*, thickness of a membrane; *m*, mass of a hydrogen molecule; *n*, concentration of chemisorbed hydrogen atoms; *P*, pressure of molecular hydrogen; *R*, particle radius; *r*, radial coordinate reckoned from the particle center; *T*, temperature; *t*, time; *X*, coordinate along the axis directed normally to the membrane surface; θ, angle between the trajectory of the molecule escaping from the surface and a normal to the latter. Subscripts: a, adsorption; eq, equilibrium; r, recombination; 0 and *L*, values of parameters at $X = 0$ and $X = L$. Superscripts: + and −, hydrogen source and sink; *, excited particles.

REFERENCES

1. G. A. Mesyats and M. D. Prokhorov, Hydrogen power engineering and fuel elements, *Vestn. Ross. Akad. Nauk*, **74**, No. 7, 579–597 (2004).
2. P. L. Andrew and A. A. Haasz, Models for hydrogen permeation in metals, *J. Appl. Phys.*, **72**, 2749–2757 (1992).
3. A. A. Pisarev and O. V. Ogorodnikova, Elementary processes near the interface between hydrogen gas and solid, *J. Nucl. Mater.*, **248**, 52–59 (1997).

4. O. V. Ogorodnikova, Comparison of hydrogen gas–, atom– and ion–metal interactions, *J. Nucl. Mater.*, **277**, 130–142 (2000).
5. A. I. Livshits, Superpermeability of solid membranes and gas evacuation, Pt. I. Theory. *Vacuum*, **29**, 103–112 (1979).
6. A. I. Livshits, F. Sube, M. N. Solovyev, M. E. Notkin, and M. Bacal, Plasma driven superpermeation of hydrogen through group Va metals, *J. Appl. Phys.*, **84**, 2558–2564 (1998).
7. L. Pranevicius, C. Templier, L. L. Pranevicius, and D. Milcius, Influence of surface barriers on hydrogen storage in MgAl films on permeable stainless steel membranes, *Vacuum*, **78**, 367–373 (2005).
8. H. Rottke and K. H. Welge, State-selective resonant excitation–ionization of H_2 with tunable VUV laser light, *Chem. Phys. Lett.*, **99** (5–6), 456–460 (1983).
9. Y. Itikawa and N. Mason, Rotational excitation of molecules by electron collisions, *Phys. Rep.*, **414**, 1–41 (2005).
10. V. V. Levdanskii, On the influence of the difference in times of adsorption on gas flows in capillaries, *Inzh.-Fiz. Zh.*, **31**, No. 1, 97–100 (1976).
11. V. V. Levdanskii, Toward the problem of laser radiation-induced mass transfer of rarefied gases in capillaries, *Zh. Tekh. Fiz.*, **52**, Issue 4, 826–827 (1982).
12. V. V. Levdanskii, Concerning light-induced drift of gas particles through a solid membrane, in: *Heat- and Mass Transfer. From Theory to Practice* [in Russian], ITMO AN BSSR, Minsk (1984), pp. 52–54.
13. A. Gross, Reactions at surfaces studied by ab initio dynamics calculations, *Surface Sci. Rep.*, **32**, 291–340 (1998).
14. N. V. Petrova, I. N. Yakovkin, and Yu. G. Ptushinskii, Monte-Carlo simulation of kinetics of H_2 molecular adsorption, *Surface Sci.*, **497**, 349–355 (2002).
15. T.-Y. Zhang and Y.-P. Zheng, Effects of absorption and desorption on hydrogen permeation. I. Theoretical modeling and room temperature verification, *Acta Mater.*, **46**, 5023–5033 (1998).
16. Y.-S. Park, J-Y. Kim, and J. Lee, Angular distribution of D_2 in thermal desorption from Si(100), *J. Chem. Phys.*, **98**, 757–758 (1993).
17. V. V. Levdansky, Gas pressure on the surface of condensed phase in a resonance radiation field, *Int. J. Heat Mass Transfer*, **42**, 4055–4063 (1999).
18. A. Pisarev, K. Miyasaka, and T. Tanabe, Permeation of hydrogen through tantalum: influence of surface effects, *J. Nucl. Mater.*, **317**, 195–203 (2003).
19. V. G. Bozhkov, V. A. Kagadei, D. I. Proskurovskii, and L. M. Romas', A comparative investigation of the penetration of atomic hydrogen into thin vanadium films and into the silicon oxide–gallium arsenide system, *Pis'ma Zh. Tekh. Fiz.*, **26**, Issue 20, 68–74 (2000).
20. V. V. Levdansky, J. Smolik, and P. Moravec, Trapping of impurity molecules in condensation from mixture of gases, *Int. J. Heat Mass Transfer*, **43**, 629–637 (2000).
21. V. V. Levdansky, J. Smolik, and P. Moravec, Trapping of molecules by aerosol particles in physical and chemical deposition, *Int. Commun. Heat Mass Transfer*, **30**, 545–552 (2003).
22. V. V. Levdanskii, Dependence of the condensation (sticking) coefficient on the radius of small aerosol particles, *Inzh.-Fiz. Zh.*, **75**, No. 4, 18–22 (2002).
23. A. Zuttel, P. Wenger, P. Sudan, P. Mauron, and S. Orimo, Hydrogen density in nanostructured carbon, metals and complex materials, *Mater. Sci. Eng.*, **B108**, 9–18 (2004).
24. S. Kishore, J. A. Nelson, J. H. Adair, and P. C. Eklund, Hydrogen storage in spherical and platelet palladium nanoparticles, *J. Alloys Compd.*, **389**, 234–242 (2005).
25. M. T. Swihart, Vapor-phase synthesis of nanoparticles, *Current Opinion in Colloid and Interface Science*, **8**, 127–133 (2003).