ISSN 1063-7842, Technical Physics, 2011, Vol. 56, No. 1, pp. 30–37. © Pleiades Publishing, Ltd., 2011.
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THEORETICAL
AND MATHEMATICAL PHYSICS

Features of Excitation of the Hydrogen (Deuterium)–Metal System by an Electron Bunch

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Received June 8, 2010

Abstract—We report on the results of mass-spectroscopic analysis of the hydrogen yield from metals saturated with hydrogen under the action of accelerated electrons (with an energy of up to 100 keV and a current density from 3 to 30 μA). It is found that the desorption rate is determined not only by parameters of the electron bunch, but also by the structure of the oxide film. It is discovered that the electronic subsystem of hydrogen-enriched metals enhances their ability to absorb the energy of the external electromagnetic action and to preserve it for a longer time as compared to a pure metal. This facilitates nonequilibrium migration and yield of hydrogen under the action of radiation in the subthreshold range. A theoretical model is proposed and analytic dependences are derived for the intensity of hydrogen yield from metals exposed to an electron bunch. The results of this study can be used for the removal of hydrogen from metals and for obtaining submicrocrystalline materials (e.g., titanium).

DOI: 10.1134/S1063784211010051

INTRODUCTION: FORMULATION OF THE PROBLEM

It is well known that hydrogen introduced into a metal radically changes its properties [1]. Since the time of publication [1], a large number of works dealing with problems classified by Yu.M. Kogan (who was the editor of translation [1]) as fundamental have appeared. Subsequent publications discussed in reviews [2, 3] were devoted to the solution of these problems. In particular, it was found that nonequilibrium thermodynamic systems that cannot be synthesized by traditional methods can be obtained by controlling the hydrogen concentration in the bulk of solids with the help of irradiation [3–6]. These problems have become topical in recent years for researchers engaged in various fields of science [3–8] because a deep and controllable rearrangement of metals and alloys can be carried out at various levels of their structure [3, 9].

The electronic subsystem of MeH_x compounds (Me stands for a metal) effectively absorbing the energy of radiation passes to an excited state. The frequency of collective oscillations of the hydrogen subsystem does not belong to the background spectrum of the crystal lattice of the metal; for this reason, its relaxation is hampered. Under the action of an electron bunch in the subthreshold range, hydrogen atoms begin to drift intensely over the crystal and can leave the boundaries of the metal. This indicates a manifestation of collective properties of the internal hydrogen atmosphere and is reflected in some nonlinear effects, in particular, in the dependences of the release rate, diffusion coefficients, and energy of hydrogen (deuterium) atoms on the density and energy of the exciting electron bunch. It was found that the hydrogen subsystem, which preserves the supplied energy for a long time over the electron relaxation time scale in metals, can stimulate the processes of accelerated diffusion and nonequilibrium release of hydrogen under the action of radiation [4, 5, 9].

This study aims at determining the optimal conditions for hydrogen removal from analysis of the yield of hydrogen (deuterium) from metals under the action of ionizing radiation in the subthreshold range and at constructing a model of hydrogen release from metals.

EXPERIMENTAL SETUP

Processes of deuterium migration and release from stainless steel, niobium, and palladium under the action of accelerated electrons were studied with the help of mass spectroscopy on a high-vacuum setup ($P_{res} \leq 10^{-5}$ to 10^{-6} Pa). The setup included a programmed heating device, a vacuum cell for sample heating and irradiation, and a vacuum tube connecting the cell to the mass spectrometer. To stimulate the nonequilibrium release of deuterium, we used an electron bunch with an energy of 10–100 keV and a current density from 3 to 500 μA, which is formed by an electron gun and a focusing magnet, as well as the beam from the electron microscope. The sample was placed into a vacuum chamber shut off from the electron gun and from the mass spectrometer by a shutter.

Metal samples were saturated with deuterium electrolytically. The saturation of stainless steel lasted for

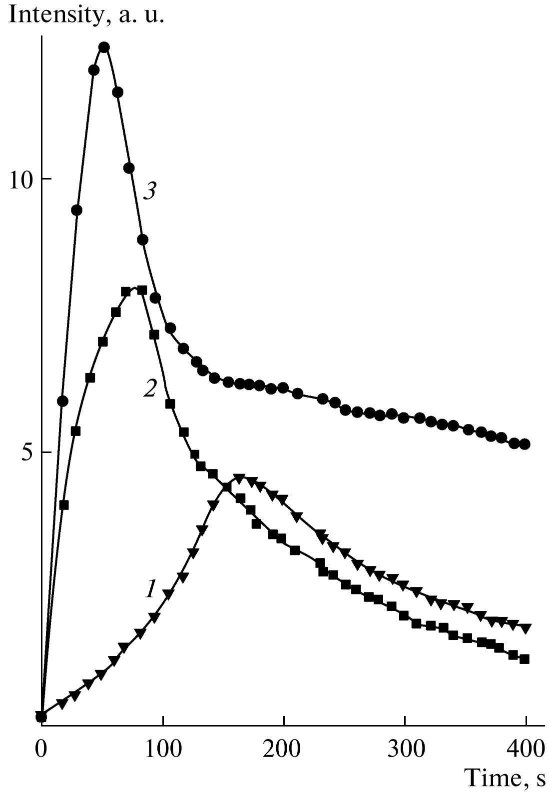

Fig. 1. Intensity of deuterium release from stainless steel under the action of an electron bunch with current I, μA: 50 (*1*), 100 (*2*), and 150 (*3*); $E = 20$ keV.

1 h for an electrolysis current density j = 1 A/cm^2; the corresponding parameters were 1 h and j = 100 mA/cm^2 for niobium and 30 min and j = 10–100 mA/cm^2 for palladium. The samples in the vacuum cell with separated cathode and anode spaces were placed on a copper heat conductor. Palladium samples were saturated with deuterium by electrolysis in a 0.3M-solution of LiOD in D_2O with a Pt anode at an electrolysis current density of j = 10 mA/cm^2 at a temperature of ~279 K. Deuterium released from metals was detected using the time-of-flight mass spectrometer that permitted continuous observation of the current from the lines of the mass spectrum.

DISCUSSION OF EXPERIMENTAL RESULTS

The kinetic curves of gas release from 12Kh18N10T stainless steel, palladium, and niobium are shown in Figs. 1 and 2. In all figures, the concentration of deuterium in the vacuum chamber measured by the mass spectrometer prior to irradiation by an electron bunch was set as zero; the increase in the hydrogen level in the vacuum chamber relative to zero is laid on the ordinate axis. In our experiments, the temperature of the outer surface of the sample in the region of action of the electron bunch was not higher than 60°C, while the temperature of its rear side was 40°C. At this temperature, the equilibrium yield of deuterium without irradiation is insignificant [1].

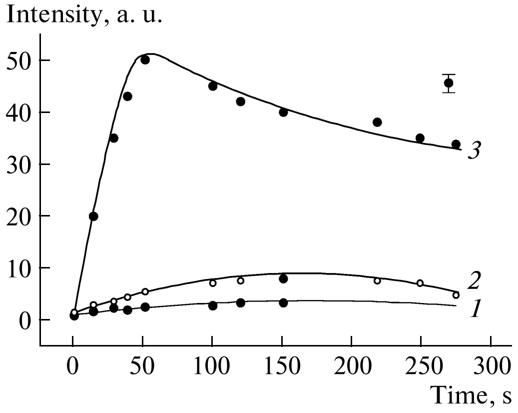

Fig. 2. Intensity of deuterium release from niobium under the action of an electron bunch with current I, μA: 50 (*1*), 100 (*2*), and 150 (*3*); $E = 20$ keV, $T = 230$°C.

It was found that the rate of excitation of hydrogen-saturated materials increases nonlinearly with the current in the stimulating electron bunch (Fig. 3), the nonlinearity in the rate of deuterium release in palladium being more pronounced as compared to niobium and stainless steel (Figs. 1, 2, 4, 5). Gas release from niobium begins under the action of the electron bunch on the sample heated to 230°C, which is due to a high energy of activation of deuterium removal from niobium [1, 4].

The effect of radiation-induced release of deuterium under the action of an electron bunch is manifested most clearly in palladium (Fig. 4). The intensity of deuterium release from Pd under the action of the electron bunch sharply increases (Fig. 5), also radiation-induced heating of palladium in the region of action of the electron bunch does not exceed 40°C. It is well known that the equilibrium heating of Pd to 40°C is not accompanied by a noticeable increase in the rate of deuterium removal from it [1]. Thus, the energy supplied under these conditions is spent by the hydrogen subsystem for removal of deuterium from the metal. This is confirmed by the data on isotope yield from metals as a function of the electron bunch energy. The bunch energy varied from 10 to 100 keV. The current in the electron bunch was 3–6 μA. The power supplied by the electron bunch was constant (IU = const). Here, U is the accelerating voltage and I is the bunch current.

The curves describing the intensity of release of deuterium from palladium as a function of the exposure time under the action of an electron bunch with different energies (Fig. 6) show that the decrease in the deuterium release intensity is faster the lower the energy of accelerated electrons. This is due to the following two factors: low-energy electrons are absorbed

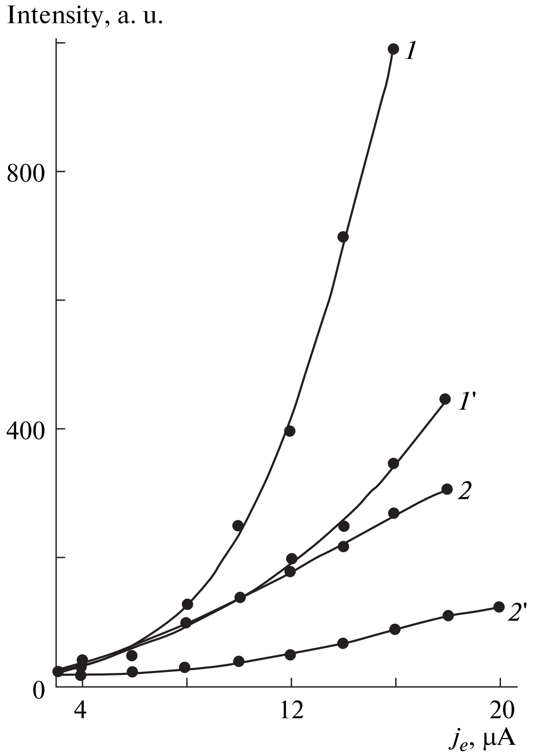

Fig. 3. Intensity of deuterium release from palladium as a function of the current in the electron bunch with an energy of 50 keV: initial surface (*1*', *2*'), developed surface (*1*, *2*). Sample temperature: 200 (*1*, *1*') and 300 K (*2*, *2*').

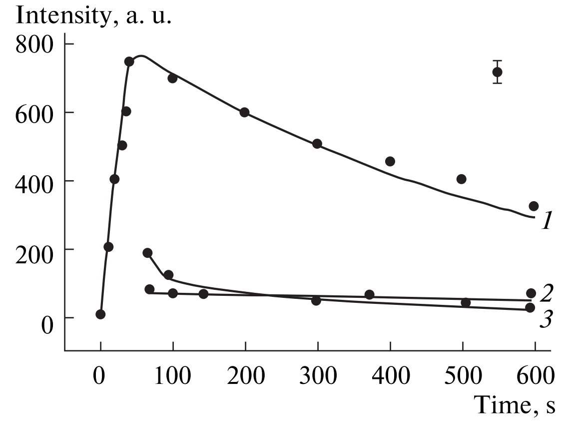

Fig. 4. Intensity of deuterium release from palladium under the action of electron bunch with current I, μA: 20 ($E = 20$ keV) (*1*), 6 ($E = 40$ keV) (*2*), and 3 ($E = 80$ keV) (*3*).

more effectively by a thin (200 nm) surface layer of palladium saturated with deuterium and stimulate intense release of deuterium from the sample. Upon a decrease in the deuterium concentration in the surface layer, the rate of deuterium release from the metal decreases. Upon an increase in the bunch energy (curve *2*), electrons penetrate to a larger depth and stimulate the release of deuterium from remote regions in the bulk of palladium. At an energy of 80 keV, the rate of variation of the gas release intensity was close to the rate of the decrease in the intensity for equilibrium release of deuterium from palladium. However, the intensity of deuterium release in this case is twice the intensity in the case of thermal stimulation, although the temperature of the Pd sample face subjected to the action of the electron bunch did not exceed 60°C.

To clarify the role of thermal energy and to eliminate its effect on the deuterium release from metals, it is important to trace the variation in the rate of the deuterium release from a metal under simultaneous action of the electron bunch and linear heating (Fig. 5). The area of the electron bunch cross section (20 mm^2) was chosen much smaller than the area of the samples (200–400 mm^2). Linear heating with simultaneous action of the electron bunch was accompanied by a shift in the position of the peak of the deuterium flux from palladium to the low-temperature region in all samples. The electron penetration depth R in palladium at energies of 40 and 80 kV was 2.5×10^{-3} and 1.0×10^{-2} mm, respectively [3]. The thickness of the palladium sample was $d = 0.015$ mm. In all cases, $R < d$; i.e., the region of direct excitation does not cover the entire volume of the sample. The power supplied by the bunch is $P = IU = \text{const}$. The peak of gas release for stainless steel under linear heating corresponds to 180°C without an electron bunch and to 80°C with the bunch; analogous temperatures are 475 and 350°C for niobium and 150 and 85°C for palladium, which corresponds to the data from [1].

It is well known that heterostructures in the form of surface oxide films may substantially change the hydrogen release from metals [1]. Figure 3 shows the deuterium gas release rate from the initial and developed surfaces of palladium as a function of the electron bunch current. Measurements were taken at palladium temperatures of 200 and 300 K. Metallic palladium was placed on a copper substrate cooled by liquid nitrogen. The electron bunch energy was 50 keV and the bunch cross-sectional area was ~0.07 cm^2. At a lower temperature, the intensity of deuterium flow from palladium increases with the bunch current at a higher rate. Such a behavior can be explained by the fact that during irradiation at a low temperature, the drift of deuterium from the surface region of the sample to its bulk is hampered. This leads to a higher density of deuterium excitation in the surface region at a low temperature. In addition, such behavior can be explained by a high gradient in the deuterium concentration in the direction from the surface to the bulk. The deuterium yield from the developed palladium surface (Fig. 3, curves *1*, *2*) is approximately thrice the yield from the initial surface (Fig. 3, curves *1*', *2*').

At a low temperature, the rate of D_2 release from Pd is higher than that at a high temperature. The concentration of D_2 at a low temperature at the Pd surface

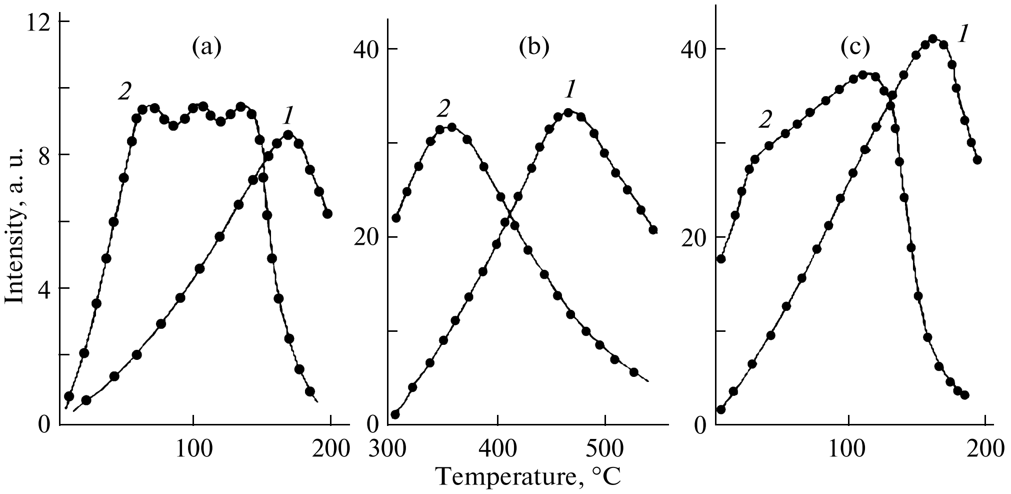

Fig. 5. Intensity of deuterium release from (a) 12Kh18N10T stainless steel, (b) Nb, and (c) Pd in the linear heating regime at a rate of 0.4 K/s: without electron bunch (*1*) and with electron bunch, $E = 20$ keV: $I = 100$ (a), 50 (b), and 20 μA (c).

(the layer thickness does not exceed 50 nm) is higher than at a high temperature. The excitation depth for palladium in this temperature range is the same and is determined by the bunch energy rather than by the bunch current. It is well known that heterostructures in the form of surface oxide films may considerably modify the hydrogen release from metals [1]. This result is reflected in Fig. 7 in the form of a stepwise variation of the deuterium flux intensity and leads to the preliminary conclusion concerning either the participation of deuterium in the formation of clusters at dislocations [1] or anomalous collective processes of excitation of the internal hydrogen atmosphere in metals by an electron bunch.

In particular, in spite of the fact that the cross-sectional area of the electron bunch is much smaller than the cross-sectional area of the entire sample, deuterium is released at a low temperature from the entire volume of the sample and not only from the region subjected to the action of the electron bunch. Such behavior of hydrogen isotopes in metals is associated with lowering of the potential barrier for the release of hydrogen from the metal into vacuum, including the

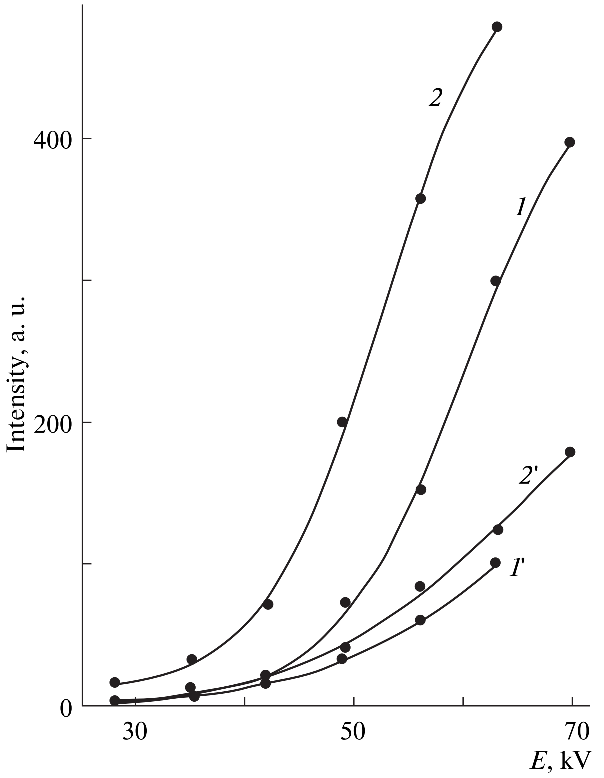

Fig. 6. Intensity of deuterium release from palladium versus the electron bunch energy ($I = 1$ μA). The sample temperature is 200 (*1*, *1'*) and 300 K (*2*, *2'*). Curves *1'* and *2'* correspond to the initial surface and curves *1* and *2* to the palladium surface after prolong action of an alkali electrolyte (developed surface).

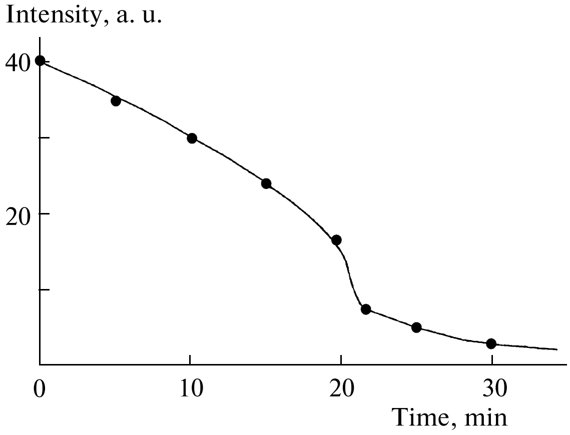

Fig. 7. Intensity of deuterium release from the heterostructure of palladium with a surface oxide film 150 nm in thickness.

processes of D^+ neutralization in the region of localization of the electron bunch. Effective propagation of excitation in the hydrogen subsystem of metals over the entire volume of the sample also takes place.

Another reason for accelerated or retarded release of hydrogen is a decrease or an increase in the surface potential barrier. Such a barrier hampers the emission of deuterons (protons) from the bulk of a metal. To verify this hypothesis, we performed experiments on stimulation (suppression) of the release of deuterium from metals upon a change in the surface barrier. For this purpose, palladium saturated with deuterium was brought in mechanical contact with an unsaturated sample of palladium annealed in ultrahigh vacuum (until the gas release ceased from it). It was found that for the positive polarity at the deuterium-saturated sample and negative polarity at the unsaturated sample, deuterium drifts intensely to the unsaturated palladium sample. The rate of this drift is determined by the magnitude and sign of the surface potential barrier and by the deuterium concentration in the saturated sample.

If the surface of palladium unsaturated with deuterium and hydrogen is oxidized (under heating to 850°C), no drift of deuterium and hydrogen to unsaturated palladium through the PdD–PdO–Pd junction is observed. If, however, the surface of saturated Pd is subjected to reduction, deuterium and hydrogen effectively drift to the unsaturated sample. These data indicate a considerable effect of the metal (palladium) oxide layer on the transport of hydrogen isotopes between contacting metals.

ANALYTIC APPROXIMATION OF NONEQUILIBRIUM RELEASE OF HYDROGEN FROM METALS

Our experimental results make it possible to consider the phenomenological model of the release of atomic hydrogen from a metal under irradiation. The balance of excited and unexcited H-bonds can be described by the system of differential equations [9]

$$\begin{cases} V\dfrac{dn_{\mathrm{H}}}{dt} = -Sv_0 n_{\mathrm{H}}; \\ V_{\mathrm{exc}}\dfrac{d\overset{v}{n}_{\mathrm{H}}}{dt} \\ = \sigma_e j_e n_{\mathrm{H}} V_{\mathrm{exc}} - S(\overset{v}{v}_{\mathrm{H}} + v_0 + \overset{v}{\nu}_{\mathrm{H}} L_{\mathrm{ex}})\overset{v}{n}_{\mathrm{H}} - V_{\mathrm{exc}}\dfrac{\overset{v}{n}_{\mathrm{H}}}{\tau_{\mathrm{rel}}}, \end{cases}$$

where V is the volume of the entire metal sample containing hydrogen, $V_{\mathrm{exc}} = L_{\mathrm{ex}}S$ is the excited volume, τ_{rel}^{-1} is the relaxation rate for excited H-bonds, $\overset{v}{v}_{\mathrm{H}}$ is the velocity of nonequilibrium migrations of atoms, and v_0 is the velocity of equilibrium migration of atoms. $\overset{v}{\nu}_{\mathrm{H}} L_{\mathrm{ex}}$ is the rate of nonequilibrium desorption of hydrogen atoms, σ_e is the cross section of excitation of H-bonds by the electron bunch, and $\overset{v}{n}_{\mathrm{H}}$ and n_{H} are the concentrations of excited and unexcited H-containing bonds. The H-bonds are excited by the electron bunch with current density j_e which is absorbed in a surface region of area S and penetrates to depth L_{ex}.

The first equation describes the "departure" of H atoms from the entire volume of the metal to the region excited by radiation. The solution to this equation has the form

$$n_{\mathrm{H}}(t) = n_0\exp\left(-\frac{Sv_0}{V}t\right).$$

The second equation describes the balance of excited H-bonds in the region of action of the exciting bunch. The solution to the second equation has the form

$$\overset{v}{n}_{\mathrm{H}} = \frac{\sigma_e j_e n_0}{\dfrac{1}{\tau} + \dfrac{1}{\tau_{\mathrm{rel}}} - \dfrac{Sv_0}{V}}\left[e^{-\frac{Sv_0}{V}t} - e^{-\left(\frac{1}{\tau} + \frac{1}{\tau_{\mathrm{rel}}}\right)t}\right],$$

where

$$\frac{1}{\tau} = \frac{\overset{v}{v}_{\mathrm{H}} + v_0 + L_{\mathrm{ex}}\nu_{\mathrm{H}^{v}}}{L_{\mathrm{ex}}}$$

is the rate of departure of H atoms from the excited region.

The flux of nonequilibrium-desorbed H atoms can be written as

$$I = L_{\mathrm{ex}}S\overset{v}{\nu}_{\mathrm{H}}\overset{v}{n}_{\mathrm{H}} = \frac{L_{\mathrm{ex}}S}{\tau_{\mathrm{des}}}\overset{v}{n}_{\mathrm{H}}.$$

For $|r_{1,2}|t \ll 1$, the flux of hydrogen atoms increases linearly with time:

$$I(t) = \sigma_e j_e S_i L_{\mathrm{ex}}\overset{v}{\nu}_{\mathrm{H}} n_0 t.$$

The nonequilibrium desorption rate $L_{\mathrm{ex}}\overset{v}{\nu}_{\mathrm{H}}$ depends on excitation level j_e; therefore, the dependence of I on j_e is generally nonlinear beginning from "small" values of t.

For $t\left(\dfrac{1}{\tau_{\mathrm{rel}}} + \dfrac{1}{\tau}\right) \gg 1$, $I(t)$ decreases in accordance with the exponential law

$$I(t) = \frac{\sigma_e j_e n_0 \overset{v}{\nu}_{\mathrm{H}}}{\dfrac{1}{\tau} + \dfrac{1}{\tau_{\mathrm{rel}}}} L_{\mathrm{ex}} S e^{-\frac{Sv_0}{V}t}.$$

If the yield of H atoms to the excited region is of diffusion nature with the law of variation $n_{\mathrm{H}} = n_{\mathrm{H}}(t)$, we obtain

$$I(t) = \frac{\sigma_s j_e \overset{v}{\nu}_{\mathrm{H}}}{\dfrac{1}{\tau} + \dfrac{1}{\tau_{\mathrm{rel}}}} L_{\mathrm{ex}} S n_{\mathrm{H}}(t).$$

If hydrogen atoms in the bulk of the metal are rigidly fixed, the variation $n_H(t)$ is controlled by diffusion processes,

$$n_H(t) \simeq n(0)\exp\left(\frac{t}{\tau_0}\right)\operatorname{erfc}\sqrt{\frac{t}{\tau_D}},$$

where τ_D is the mean time of diffusion jumps in the hydrogen subsystem, $\tau_D = L_D^2/D$, L_D being the diffusion jump length and D, the diffusion coefficient.

For a small excitation depth ($L < L_D^v$), the hydrogen yield from a bulk sample is mainly of equilibrium nature ($\tau_D = D/v_D^2$):

$$n(t) = n_0 e^{\frac{1}{\tau_D}}\operatorname{erfc}\sqrt{\frac{t}{\tau_D}}.$$

If a thin sample is excited ($v_D^{\text{eff}} d/2D^{\text{eff}} \ll 1$), the hydrogen yield at the surface is of the nonequilibrium type:

$$n(t) = n_0\exp\left(-\frac{2v^{\text{eff}}}{d}t\right),$$

The kinetic dependences of the hydrogen yield at the surface make it possible to find the flux of desorbed hydrogen molecules under the action of radiation.

In the case of a thin sample excited almost over the entire thickness, we obtain

$$n(t) = n_0\exp\left(-\frac{t}{\tau_1}\right).$$

where

$$\frac{1}{\tau_1} = \frac{2v_{\text{D}}^{\text{eff}}}{d}.$$

The flux of desorbed H_2 molecules upon irradiation of a hydrogen-saturated sample can be written in the form

$$I = (\nu'_3 N_2 + \Gamma_4 N_2^v) = \left(\nu'_3\frac{\Gamma_2\Gamma_4}{\Gamma_3+\Gamma_4}\right)N_2(t),$$

where Γ_2 is the rate of vibrational excitation of H_2 molecules adsorbed at the surface by radiation, Γ_3 is the rate of relaxation of excited hydrogen molecules, Γ_4 is the rate of nonequilibrium desorption of vibration-excited hydrogen molecules, and $N_2(t)$ is the concentration of adsorbed molecules,

$$N_2(t) = \frac{n_0 v_{\text{D}}^{\text{eff}}}{\frac{1}{\tau_2} - \frac{1}{\tau_1}}\left[\exp\left(-\frac{t}{\tau_1}\right) - \exp\left(-\frac{t}{\tau_2}\right)\right].$$

For t/τ, $t/\tau_1 \ll 1$, the flux increases linearly with time,

$$I(t) = \left(\nu'_3\frac{\Gamma_2\Gamma_4}{\Gamma_3+\Gamma_4}\right)n_0 v_{\text{D}}^{\text{eff}} t$$

and attains its maximal value at instant

$$t_{\max} = \frac{\tau_1\tau_2}{\tau_2-\tau_1}\ln\frac{\tau_2}{\tau_1}.$$

For a bulk sample ($d \gg 2D/v_D^v$), the change in the concentration of molecules at the surface under excitation has the form

$$\frac{dN_2(t)}{dt} = v_d^{\text{eff}} n_0 e^{\frac{1}{\tau_{\text{D}}^{\text{eff}}}}\operatorname{erfc}\sqrt{\frac{t}{\tau_D^{\text{eff}}}} - \frac{1}{\tau_2}N_2(t).$$

The solution to this equation was obtained using the Laplace transformation:

$$N_2(t) = \frac{n_0 v_D^{\text{eff}}}{\frac{1}{\tau_D^{\text{eff}}} + \frac{1}{\tau_2}}\left[e^{\frac{1}{\tau_D^{\text{eff}}}}\operatorname{erfc}\sqrt{\frac{t}{\tau_D^{\text{eff}}}}\right.$$

$$\left. - i\sqrt{\frac{\tau_2}{\tau_D^{\text{eff}}}}e^{-\frac{t}{\tau_2}}\operatorname{erfc}\left(i\sqrt{\frac{t}{\tau_2}}\right) - e^{-\frac{t}{\tau_2}}\right],$$

For “small” t ($t/\tau_D^{\text{eff}} \ll 1$, $1/\tau_2 \ll 1$), we obtain

$$I(t) = \left(\nu'_3 + \frac{\Gamma_2\Gamma_4}{\Gamma_3+\Gamma_4}\right)n_0 v_D^{\text{eff}}\left(1 - \frac{5}{3}\sqrt{\frac{t}{\tau_D^{\text{eff}}}}\right)t.$$

Thus, the increase in the intensity is determined by the nonequilibrium yield and desorption of molecules, but is suppressed by diffusion-controlled depletion of the surface layer of the sample.

For “large” t ($t/\tau_2 \gg 1$, $t/\tau_D^{\text{eff}} \gg 1$), the desorption of molecules is limited by diffusion:

$$I(t) = n_0\sqrt{\frac{D^{\text{eff}}}{4\pi t}}.$$

Approximation of experimental curves by calculated dependences makes it possible to determine the parameters of nonequilibrium diffusion and release of hydrogen from metals. Using the second-order Runge–Kutta method in the model of random walks of atoms, we can calculate the main parameters of hydrogen desorption. The parameters required for calculations were borrowed from [1, 4, 9, 10]. For example, for a palladium sample at a temperature of 40°C and for an electron bunch current of 20 μA, calculations give

$$(\tau_D^{\text{eff}})^{-1} \approx 6.3 \times 10^{-2} s^{-1}; \quad \tau_2^{-1} \approx 0.1\ \text{s}^{-1}.$$

The approximating curve (solid curve corresponds to calculations and dots are experimental results) is curve *1* in Fig. 4. The ratio of the diffusion coefficients for palladium with and without excitation by an electron bunch is ($D^{\text{eff}}/D \approx 1.4$). This ratio corresponds to accelerated diffusion flux of deuterium from the Pd surface. Accordingly, in the near-surface region, higher concentrations of deuterium were attained,

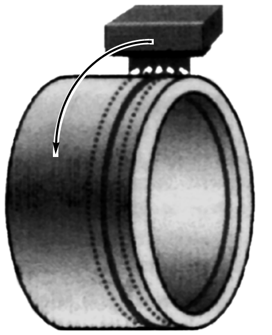

Fig. 8. Schematic diagram of hydrogen removal from an article under irradiation by an electron bunch.

which increases the frequency of local vibrations $\omega \propto \sqrt{n_D}$ and D_{eff}.

In experiments with Pd–H and D, the H_2 flux decreases during prolonged gas release in proportion to $\propto t^{-1/2}$, which is typical of bulk samples (with $d > L_D^v$).

Similar kinetic dependences $\propto t^{-1/2}$ on the ascending segment of the $I(t)$ curve were observed for stainless steel. The kinetic curves of H_2 gas release for stainless steel are characterized by the following parameters (see Fig. 1):

$$50\ \mu\text{A}: (\tau_D^{\text{eff}})^{-1} = 3 \times 10^{-2}\ \text{s}^{-1}, \quad \tau_2^{-1} = 10^{-2}\ \text{s}^{-1};$$

$$100\ \mu\text{A}: (\tau_D^{\text{eff}})^{-1} = 5.1 \times 10^{-2}\ \text{s}^{-1}, \quad \tau_2^{-1} = 3 \times 10^{-2}\ \text{s}^{-1};$$

$$150\ \mu\text{A}: (\tau_D^{\text{eff}})^{-1} = 7.3 \times 10^{-2}\ \text{s}^{-1}, \quad \tau_2^{-1} = 5 \times 10^{-2}\ \text{s}^{-1}.$$

For niobium (see Fig. 2), we have

$$50\ \mu\text{A}: (\tau_D^{\text{eff}})^{-1} \le 6 \times 10^{-4}\ \text{s}^{-1}, \quad \tau_2^{-1} \le 1.5 \times 10^{-2}\ \text{s}^{-1};$$

$$100\ \mu\text{A}: (\tau_D^{\text{eff}})^{-1} = 8 \times 10^{-2}\ \text{s}^{-1}, \quad \tau_2^{-1} = 3 \times 10^{-2}\ \text{s}^{-1};$$

$$150\ \mu\text{A}: (\tau_D^{\text{eff}})^{-1} = 3 \times 10^{-3}\ \text{s}^{-1}, \quad \tau_2^{-1} = 5 \times 10^{-2}\ \text{s}^{-1}.$$

The rates of effective diffusion $(\tau_D^{\text{eff}})^{-1}$ and nonequilibrium desorption τ_2^1 increase nonlinearly upon an increase in the current density in the electron bunch.

Thus, having selected the parameters of electron bombardment and its duration and using the calibration curves, we can carry out technological processes associated, for example, with the removal of hydrogen from metals.

Figure 8 shows the schematic diagram for technological removal hydrogen from an article (made of stainless steel) upon irradiation by an electron bunch. The regime of hydrogen removal is controlled by the parameters of irradiation (see Fig. 1), while the residual hydrogen concentration can be determined using the calibration curve. At present, the formation of a submicroscopic structure of metals [11] including the reverse doping of hydrogen is a topical problem. This process must occur at a low temperature (350°C). "Cold" removal of hydrogen from titanium upon electron bombardment makes it possible to obtain articles of titanium and its alloys with a submicrometer structure. This is due to the fact that the removal of hydrogen [1] is accompanied by coarsening of metal grains, which lowers the plasticity of the material.

CONCLUSIONS

Diffusion of hydrogen and deuterium at a rate noticeably exceeding the rate of thermal-equilibrium diffusion of H and D in metals may occur in the presence of the long-lived (on the time scale of one-phonon and electron relaxation) vibration-excited H, D subsystem in metals. The excited hydrogen subsystem in metals stimulates diffusion not by the energy of thermal fluctuation (kT), but by the excess energy of nonequilibrium vibrations ($\hbar\omega_H$) in the hydrogen subsystem of metals, which is fed by external ionizing radiation. In this case, effective diffusion coefficient $D_0\exp(-E_{\text{act}}/\hbar\omega_H)$ and effective diffusion rate D_H/kT may considerably exceed their equilibrium values $D_0\exp(-E_{\text{act}}/kT)$.

The energy of nonequilibrium vibrations depends on concentration n_H of hydrogen atoms in the metal and is given by $\hbar\omega_H = \hbar e\sqrt{n_H/m_p\varepsilon_0}$. In the model of plasma oscillations of hydrogen isotopes in a metal, collective properties of intrinsic hydrogen atmosphere are manifested explicitly. The ratios of the equilibrium and effective nonequilibrium diffusion coefficients are constant ($D_H^{\text{eff}}/D > 1.4$ for H in Pd). An increase in the plasma oscillation frequency upon an increase in the concentration of hydrogen introduced in the samples explains the nonlinear effects in the dependence of the density of radiation-induced flow of hydrogen isotopes from metals on the concentration of hydrogen introduced into them.

The nonlinearity in the dependence of the hydrogen flux from metals on the electron bunch current can be explained (in the model discussed here) by an increase in the flux of hydrogen atoms to the surface and radiation-induced desorption of hydrogen molecules from the surface.

The effects associated with stimulation of nonequilibrium yield of protons from metals under the action of electrons can be explained by a reduction of the potential barrier for hydrogen released from the metal to vacuum. This reduction is effective under the action of an electron bunch because accelerated electrons can neutralize H^+ and D^+ ions emerging from the bulk at the surface; under the impact of H, D by an electron with an energy of several tens kiloelectronvolts, hydrogen atoms and molecules receive a sufficient amount of energy for the departure from the surface to vacuum. Photons acquire a comparable mass sufficient for a simple kinetic knock-out only for an energy of ~500 keV. In this case, the penetrability of materials to radiation is so high that the excitation of the hydrogen atmosphere becomes ineffective again.

Thus, the absorption of energy of external radiation and, accordingly, the hydrogen release from hydrogenated steel, niobium, and palladium depend on the microphysical parameters of elements of the system and on its structure (the thickness of the metal oxide layer), as well as on the position of the oxide layer in the structure, the energy and current density in the electron bunch, the concentration of introduced hydrogen, and the exposure time.

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Translated by N. Wadhwa

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