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SHORT COMMUNICATIONS

Hydrogen Diffusion in Steels under Electron Bombardment

V. V. Larionov, N. N. Nikitenkov, and Yu. I. Tyurin*
National Research Tomsk Polytechnic University, pr. Lenina 30, Tomsk, 634050 Russia
**e-mail: tyurin@tpu.ru*

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Abstract—We report on the results of measurement of the coefficients of hydrogen diffusion through metal membranes in the course of their simultaneous hydrogen saturation and bombardment with electrons (energy 30 keV, current density from 3 to 30 μA) both in a broad and in a narrow beam. It is found that the time of hydrogen discharge from the membrane is determined by the parameters of the electron beam, its periodicity and duration, and also depends on the structure of the phase state of the metal membrane. It is shown that the diffusion coefficient increases when a narrow electron beam in the scanning regime is used. Analysis of the hydrogen yield as a function of time is carried out on a mass spectrometer connected to a vacuum chamber containing an electron gun, a beam sweep oscillator, and an electrolytic cell. The hydrogen diffusion coefficients under the action of a scanning electron beam are 15 times larger than under the same conditions without irradiation.

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INTRODUCTION

Hydrogen is implanted into various structural materials used in space and nuclear technologies, as well as in articles subjected to hydrogen saturation and irradiation during their operation. This is due to the fact that owing to its high diffusion mobility in metals, hydrogen is easily redistributed in the bulk of a material and, hence, considerably changes its properties [1–3]. Diffuse transport of hydrogen in metals may produce a negative effect on the physical properties of metals and their strength characteristics. At the same time, hydrogen plays a significant role in technology of new materials [4]. Analysis of the processes under investigation in irradiation conditions is of special interest [5–7]. Under the action of an electron beam, hydrogen atoms begin to move intensely over the crystal and some of them leave it. It should be borne in mind that the concentration of hydrogen in a metal is nonuniform, and layered distribution of hydrogen concentration over a metal is observed in some cases [8–10]. The internal hydrogen atmosphere in metals exhibits collective properties, which is reflected in a number of nonlinear effects, in particular, in the dependence of the hydrogen outflow velocity, diffusion coefficients, the energy of hydrogen atoms, and on the density and energy of the exciting electron beam. The hydrogen subsystem of a metal, which preserves the supplied energy on the electron relaxation time scale for metals, can stimulate accelerated diffusion and nonequilibrium yield of hydrogen under the action of radiation [5, 8, 9, 11]. The state of hydrogen-saturated metal and the saturation with hydrogen are analyzed using various methods [10]. One such method is the determination of hydrogen diffusion coefficients. The diffusion coefficient can be determined by measuring steady-state flux $J(t)$ at the exit side of the membrane of thickness h over a prolonged time interval. For this purpose, the delay time is measured for a nonstationary state, which is defined as point t_1 of intersection of the tangent to the $J(t)$ curve with the time axis, where $J(t)$ is the hydrogen flux through the membrane; time of inflection t_2 (the time at which the second derivative changes its sign), half-wave time t_3 (i.e., the instant at which the flux attains half the steady-state value), and time t_4 at which the flux attains the steady-state regime. Using the characteristic time, we can calculate the diffusion coefficient the formulas [11]

$$D = \frac{h^2}{19.9t_1} = \frac{h^2}{10.9t_2} = \frac{h^2}{7.3t_3} = \frac{h^2}{6t_4}. \quad (1)$$

This study is aimed at determining the hydrogen diffusion coefficients from analysis of the hydrogen yield from metals under the action of ionizing radiation (narrow and broad beams) and at analysis of the model of hydrogen make from metals.

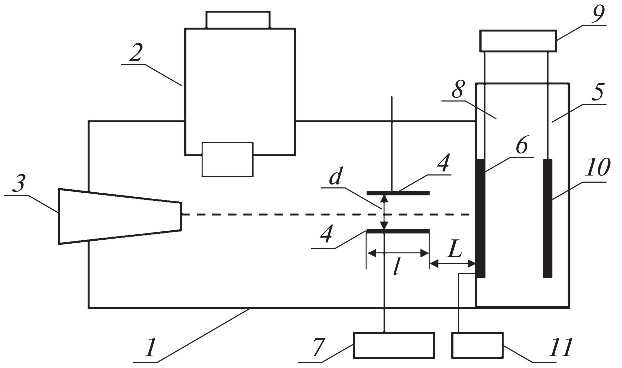

Fig. 1. Block diagram of experimental setup: (*1*) vacuum chamber; (*2*) mass spectrometer; (*3*) electron gun; (*4*) metal plates deflecting the electron beam; (*5*) electrolytic cell; (*6*) membrane (sample); (*7*) oscillator for deflecting plates; (*8*) electrolyte; (*9*) power supply; (*10*) anode of the electrolytic cell; and (*11*) microammeter.

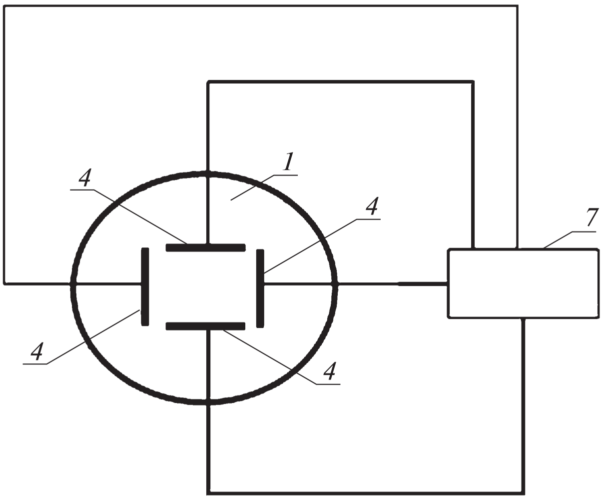

Fig. 2. Diagram of arrangement of control electrodes (notation is the same as in Fig. 1).

1. EXPERIMENTAL

The experimental setup consists of a vacuum chamber connected to a mass spectrometer (Fig. 1). The vacuum chamber contains an electron gun and a sample being saturated with hydrogen [12–14]. The electron beam is directed to the sample. The sample has the form of a planar plate. The 15-μm-thick membrane (sample) is cut from a 12Kh18N12T stainless steel plate and is inserted into chamber *1*. The chamber is a cylindrical tube of diameter 30 mm; the membrane of diameter 20–25 mm is inserted into the end of the tube. Chamber *1* is connected to electrolytic cell *5* so that the membrane separates the chamber from the cell. One side of the membrane faces vacuum chamber *1* and the other side faces the electrolytic cell. The cell is filled with 0.1M sulfuric acid solution. In contrast to [11–13], voltage U can be applied to the deflecting plates built-in into the chamber for deflecting the beam by y and x from the membrane center. The experimental setup has the following parameters: energy of beam electrons $E_0 = 30$ keV, distance from the edge of the deflecting plate $L = 20$ mm, plate length $l = 200$ mm, and the distance between the plates $d = 10$ mm. Voltage U that should be applied to the plates to deflect electrons so that they hit the membrane at distance y or x above or below the membrane center can be calculated by the formula

$$U = y\left(\frac{2dE_0}{elL}\right). \tag{2}$$

Mass spectrometer *2* is activated in the regime of analysis of the hydrogen (H_2) line, and the mass spectrum of residual gases is recorded in chamber 1 of the device containing membrane *6*, electron gun *3*, and four plates *4* deflecting the electron beam. Figure 2 shows the arrangement of four deflecting plates *4*, to which the voltage from sweep oscillator *7* is applied in vacuum chamber *1*. Constant voltage from DC SUPPLY HY 3002 source is applied to anode *10* and membrane *6*, and a current density of 1 A cm^{-2} is set with the help of a rheostat.

2. EXPERIMENTAL RESULTS AND DISCUSSION

Hydrogen saturation is accompanied with a change in the structure of the metal sample (for example, from coarse-crystalline to submicrocrystalline in titanium). It is well known [4, 11, 14] that diffusion of hydrogen in a metal depends not only on the type of the crystal lattice in the metal, but also on the degree of its perfection. Crystal lattice defects affect most strongly the diffusion coefficients and the solubility of hydrogen in the metal [14]. For this reason, it is necessary to direct the electron beam to different regions of the metal sample for exciting hydrogen in the metal with the structure varying in the course of irradiation. The use of a steady-state narrow electron beam can reduce the accuracy of measurements of the hydrogen diffusion coefficients in the metal under simultaneous electron excitation and saturation with hydrogen. It should be borne in mind that the following circumstances lead to considerable errors of measurements. During diffusion of hydrogen in a metal, it is distributed nonuniformly over the metal volume because of inhomogeneity of the metal structure. Inhomogeneities include dislocations along which hydrogen is accumulated, energy traps, and segregation cavities in which the hydrogen pressure may attain 10^4 atm [2]. At high hydrogen concentrations, metal hydrides are formed, which affect the diffusion of hydrogen [1, 10, 14, 15]. The diffusion coefficient is also affected by grain boundaries, the porosity of the material, stresses, and dynamic loads appearing during heating of the metal [1, 16]. Ultrafine-grain (nano- and sub-

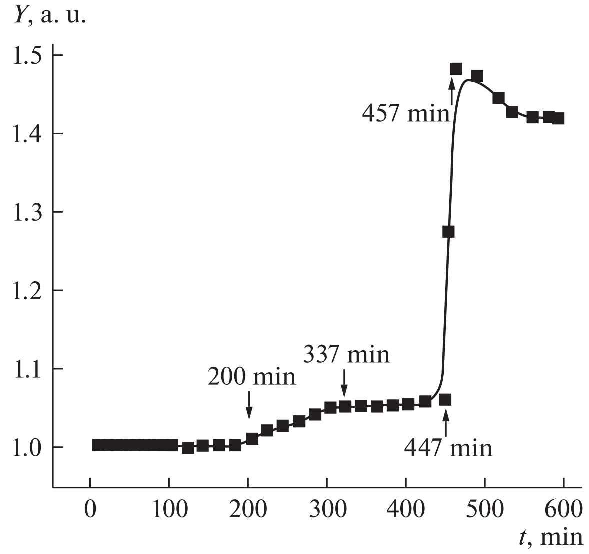

Fig. 3. Time dependence of the hydrogen yield in the case of simultaneous bombardment with electrons and saturation with hydrogen (arrows indicate time in minutes).

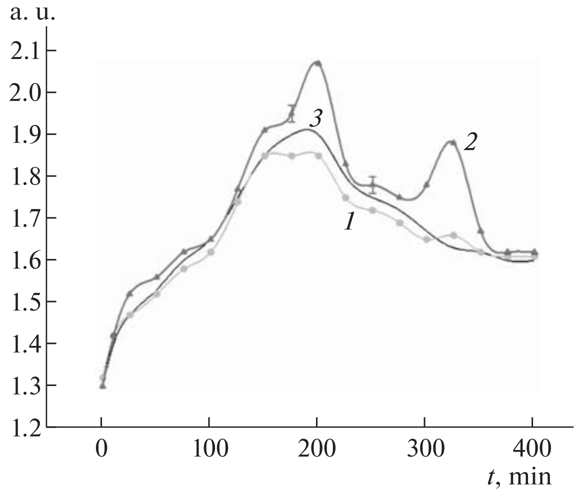

Fig. 4. Time dependences of hydrogen yield from steel with electron bombardment after the termination of saturation with hydrogen: (*1*) steady-state beam; (*2*) scanning beam; and (*3*) theoretical calculation.

micrometer) crystalline materials that have been actively developed recently differ from coarse-crystalline materials. The hydrogen diffusion coefficients in these materials differ substantially because of different grain sizes [14].

Figure 3 shows an approximate graph of the time dependence of the hydrogen yield from the membrane (in arbitrary units). The initial level of hydrogen is taken as unity; arrows indicate the following time instants; 200 min, corresponding to the attainment of the steady-state level of the H_2 concentration in the vacuum chamber (at this instant, electrolysis begins); 337 min, corresponding to the actuation of the electron beam and sweep oscillator (H_2 concentrations attains the stationary value after the beginning of electrolysis); 347 min, corresponding to the attainment of the maximal intensity under the action of the beam, and 435 min, corresponding to the attainment of the steady-state value after irradiation of the membrane. Our results make it possible to calculate the diffusion coefficient using formula (1): $D = h^2/6t_3 = 59.4 \times 10^{-14}$ m^2 s^{-1}. The error in the determination of the diffusion coefficient depends on the accuracy of fixation of the instant at which the intensity of the hydrogen line attains the steady-state value. In the conditions of the electron beam expanded with the help of the magnetic field of the gun to $d = 20$ mm, which stably irradiates the entire surface of the membrane, the maximal intensity of the hydrogen lines is lower by 40%, while time t_3 increases to 25 min and even longer. The application of a narrow electron beam in the steady-state conditions (i.e., without scanning the membrane surface) also increases the yield time t_3. The peak value of the intensities of lines is reduced thereby by 10–12%. This effect is apparently associated with the charge density redistribution in the hydrogen-saturated metal under the action of the electron beam, as well as with a nonuniform concentration of defects in the course of hydrogen saturation of the membrane.

The dependences of the hydrogen yield from steel under the bombardment with electrons after the termination of saturation with hydrogen in the stationary regime and with the scanning beam are shown in Fig. 4. Curve *2* in this figure passes above curve *1* and has an additional peak. This peak apparently appears due to the energy redistribution in the hydrogen subsystem under scanning of the beam and can be explained by a nonuniform distribution of defects at which hydrogen is accumulated in the metal.

The hydrogen diffusion coefficient is calculated in the conditions corresponding to Fig. 4 (curve *3*) in accordance with the following theoretical model [5]. Since a thin sample of thickness h ($v_H^{\text{eff}} h/2D^{\text{eff}} \ll 1$) is excited, the hydrogen flux to the surface is nonequilibrium [6]:

$$n(t) = n_0 \exp\left(-\frac{2v^{\text{eff}}}{h}t\right). \qquad (3)$$

The flux of the hydrogen molecules desorbing under the action of irradiation in the case of a thin sample excited almost over the entire depth has the form [6]

$$n(t) = n_0 \exp\left(-\frac{t}{\tau_1}\right), \quad \text{where} \quad \frac{1}{\tau_1} = \frac{2v_H^{\text{eff}}}{h}. \qquad (4)$$

The flux density of desorbing H_2 molecules under the irradiation of the hydrogen-saturated sample is calculated as

$$I = (\nu'_3 N_2 + \Gamma_4 N_2^V) = \left(V'_3 \frac{\Gamma_2 \Gamma_4}{\Gamma_3 + \Gamma_4} \right) N_2(t), \qquad (5)$$

where Γ_2 is the rate of vibrational excitation of the H_2 molecule adsorbed on the surface by radiation, Γ_3 is the rate of relaxation of excited hydrogen molecules, and Γ_4 is the rate of nonequilibrium desorption of vibrationally excited hydrogen molecules. Concentration $N_2(t)$ of adsorbed molecules is given by

$$N_2(t) = \frac{n_0 V_D^{\text{eff}}}{\frac{1}{\tau_2} - \frac{1}{\tau_1}} \left(\exp\left\{ -\frac{t}{\tau_1} \right\} - \exp\left\{ -\frac{t}{\tau_2} \right\} \right). \qquad (6)$$

For values of t such that $1/\tau$, $t/\tau_1 \ll 1$, the flux density increases linearly with time:

$$I(t) = \left(\nu'_3 \frac{\Gamma_2 \Gamma_4}{\Gamma_3 + \Gamma_4} \right) n_0 V_H^{\text{eff}} t \qquad (7)$$

and has a peak at $t = t_{\max}$:

$$t_{\max} = \frac{\tau_1 \tau_2}{\tau_2 - \tau_1} \ln \frac{t_2}{t_1}. \qquad (8)$$

For “small” t $(t/\tau_D^{\text{eff}} \ll 1, t/\tau_2 \ll 1)$, we can obtain [6]

$$I(t) = \left(\nu'_3 + \frac{\Gamma_2 \Gamma_4}{\Gamma_3 + \Gamma_4} \right) n_0 V_D^{\text{eff}} \left(1 - \frac{5}{3} \sqrt{\frac{t}{\tau_H^{\text{eff}}}} \right) t. \qquad (9)$$

Thus, the increase in the intensity is determined by the nonequilibrium yield and desorption of molecules, but is decelerated by diffusive depletion of the surface layer of the sample. The depletion effect apparently depends on the hydrogen distribution over dislocations and in accordance with their form. For “large” t $(t/\tau_2 \gg 1, t/\tau_H^{\text{eff}} \gg 1)$, when the excitation by an electron beam is extended (nonequilibrium “release” of hydrogen from the traps has occurred), the desorption of molecules is limited by the standard diffusion process $I(t) = n_0 \sqrt{\frac{D^{\text{eff}}}{4\pi t}}$. The kinetic dependences of H_2 gas release for stainless steel is proportional to $t^{-1/2}$ and is characterized by the following parameters (see Fig. 4): a wide beam $(\tau_H^{\text{eff}})^{-1} = 2 \times 10^{-2}$ s^{-1}, $\tau_2^{-1} = 10^{-2}$ s^{-1}, and a narrow beam of 40 μA with $(\tau_H^{\text{eff}})^{-1} =$ s^{-1}, $\tau_2^{-1} = 2.25 \times 10^{-2}$ s^{-1}. We observe a satisfactory coincidence of the theoretical (curve *3*) and experimental results (curves *1* and *2* in Fig. 4). The rates of effective diffusion (τ_H^{eff}) and nonequilibrium desorption τ_2^{-1} increase nonlinearly with increasing electron beam density.

Thus, choosing the parameters of electron irradiation and its duration and using the graduated curves, we can carry out technological processes associated, for example, with the removal of hydrogen from metals.

CONCLUSIONS

Hydrogen diffusion in the irradiated steel occurs with a rate higher than the rate of thermally equilibrium diffusion of hydrogen in metals. The excited hydrogen subsystem of metals stimulates the diffusion not by thermal fluctuation energy kT, but by the excess energy of nonequilibrium vibrations in the hydrogen subsystem of the metal, which is fed by external ionizing radiation. The ratio of the nonequilibrium diffusion coefficient to the corresponding equilibrium value for hydrogen in steel exceeds 15. The effects of stimulation of nonequilibrium hydrogen yield from metals under the action of electrons can be explained by lowering of the potential barrier for hydrogen escaping from the metal to vacuum. Accelerated electrons can neutralize H^+ ions emerging from the bulk to the surface, and when an electron with energy on the order of 10 keV hits hydrogen atoms and molecules, the latter acquire energy sufficient for the escape from the metal surface to vacuum. In the presence of defects at which hydrogen is accumulated, the nonequilibrium distribution of hydrogen in the sample is detected by scanning the sample with an electron beam. Thus, the absorption of energy of the external action and, accordingly, the hydrogen yield from steel saturated with hydrogen depend on microphysical parameters of the elements of the system, its structure (number of defects and their distribution over the surface of the membrane), and irradiation time.

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REFERENCES

1. *Hydrogen in Metals,* Ed. by. G. Alefeld and J. Volkl (Springer, New Yok, 1978).
2. Yu. S. Nechaev, Phys. Usp. **44**, 1189 (2001); Phys. Usp. **49**, 563 (2006); Phys. Usp. **51**, 681 (2008).
3. V. V. Ovchinnikov, Phys. Usp. **51**, 955 (2008).
4. A. A. Il’in, B. A. Kolachev, and I. S. Pol’kin, *Titanium Alloys: Composition, Structure, Properties* (VILS-MATI, Moscow, 2009).
5. Yu. I. Tyurin, N. N. Nikitenkov, and V. V. Larionov, Zh. Fiz. Khim. **85**, 1148 (2011).
6. Yu. I. Tyurin, V. V. Larionov, I. P. Chernov, and E. A. Sklyarova, Tech. Phys. **56**, 30 (2011).
7. V. N. Kudiyarov, A. M. Lider, and N. S. Pushilina, Izv. Vyssh. Uchebn. Zaved., Fiz. 56 (11/3), 132 (2013).
8. B. V. Goryachev and S. B. Mogil’nitskii, Izv. Tomsk. Politekh. Univ. **324** (2), 102 (2014).

9. B. V. Goryachev and S. B. Mogil'nitskii, Izv. Tomsk. Politekh. Univ. **322** (2), 78 (2013).
10. B. V. Goryachev and S. B. Mogil'nitskii, Izv. Tomsk. Politekh. Univ. **323** (2), 63 (2013).
11. E. A. Edvard, I. E. Gabis, and A. P. Voyt, J. Alloys Compd. 404–406, 335 (2005).
12. Yu. I. Tyurin, A. M. Semenov, and N. N. Nikitenkov, Poverkhnost, No. **5**, 90 (2004).
13. N. N. Nikitenkov, A. M. Khashkhash, I. A. Shulepov, V. D. Khoruzhii, Yu. I. Tyurin, I. P. Chernov, and E. N. Kudryavtseva, Prib. Tekh. Eksp., No. 6, 110 (2009).
14. G. P. Grabovetskaya, N. N. Nikitenkov, I. P. Mishin, I. V. Dushkin, E. N. Stepanova, and V.S. Sypchenko, Izv. Tomsk. Politekh. Univ. **322** (2), 55 (2013).
15. *Hydrogen Interaction with Metals,* Ed. by A. P. Zakharov (Nauka, Moscow, 1987).
16. A. V. Gapontsev and V. V. Kondrat'ev, Phys. Usp. **46**, 1077 (2003).

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