

Study of the Hydrogen–Metal Systems

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Hydrogen accumulation in samples of a palladium and 12Kh18N10T steel at the hydrogen charging by the electrolytic method and hydrogen release from these samples at its electron and X-ray irradiation are studied. Palladium was used as a comparison material (as most efficiently solvent hydrogen known among the simple materials). It is established that a capture effectiveness of hydrogen from an electrolyte (1 M H₂SO₄ at current density is 0.5 A cm⁻²) for palladium is 3–4 orders more than for steel. The hydrogen yield nonlinearly increases with growing of electron current density and electron energy is more than 40 keV under electron irradiation of saturated palladium and 12Kh18N10T steel samples. About 90% of the hydrogen had removed from hydrogen saturated palladium samples and only 60% from steel under electron beam with energy 40 keV and current density $\approx 20 \mu\text{A cm}^{-2}$ for 1 h of irradiation. It is necessary to increase the energy of electrons from 40 to 100 keV for the more effective removal of hydrogen.

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1. Introduction

We have studied metal–hydrogen systems and their behavior under the influence of an ionizing radiation for more than 20 years. About 200 papers and monographs were published by us on this theme in Russia predominantly.

This paper is an example of our experimental results of studying radiation-enhanced hydrogen yield from palladium and 12Kh18N10T steel. Cold removal of hydrogen from materials is an actual problem both for hydrogen and for nuclear powers [1–3]. One of methods of such hydrogen removal is action by ionizing radiation in material which contains hydrogen. Thus the material should not be heated up under the influence of the radiation. It is possible in many cases.

The goal of present work is research of hydrogen accumulation and the effect of ionizing radiation (electrons and X-rays) on the hydrogen remove from palladium and 12Kh18N10T steels. Hydrogen accumulation and its motion in the materials (especially enhanced by electrons and X-rays irradiation) promote the diffusion of defects and impurities, and in a result these are causes of the transformation of the defect structure of materials.

Palladium (as a material capable to accumulate the great hydrogen concentration) and steel (as a material not capable to accumulate the great hydrogen concentration) have been chosen for research. Besides, these materials are widely used in numerous technological applications, and accumulation of hydrogen is one of the most considerable reasons of degradation of technological properties in these materials, which gives rise to embrittlement and a drop of plasticity, especially in the regions of welded joints [1–3]. The ionizing radiation is observed now both as a perspective expedient for annealing of de-

fects in semiconductor materials and as expedient of “cold removal” hydrogen from metals.

As will be shown below, the above listed causes have an effect on temperature spectra of thermally stimulated gas release (TSGR) (the more conventional method name applicable to all atoms of solids is thermally stimulated desorption (TSD)) and the kinetics of hydrogen release from samples under electron and X-ray irradiation (radiation stimulated gas release (RSGR)). The installation [4] was used for research.

2. Materials and experimental techniques

Samples of 12H12M1BFR ferrite steel have been made from a sheet of material by a method of spark cutting in rectangular plates with sizes 25×5.0×2.0 mm³. The sizes of palladium samples were 25×5.0×0.5 mm³. All samples have been mechanically polished and annealed in vacuum furnace at temperature 750 °C within 1 h with following cooling without disturbance of the vacuum. The samples of 12H12M1BFR steel were charged by hydrogen in an electrolytic cell with 1 M H₂SO₄ solution in ordinary or heavy water at a current density of 0.5 A/cm² and saturation times from 2 to 74 h. The palladium samples have been charged by hydrogen in the same electrolyte, but at saturation time only 6 min (at major saturation times the strong hydrogen allocation in analytical installation [4] did not allow to carry out the analysis — pressure in the analytical chamber was too sweepingly sharply increased). Immediately after saturation and drying, the samples prepared in such a way were placed in a vacuum chamber to study TSGR or RSGR.

The process of hydrogen accumulation was investigated by recording of TSGR spectra (dependence of intensity of the hydrogen yield on temperature) during a linear heating of the samples after different saturation

times of samples. Further temperature spectra were integrated and constructed depending on an integrated yield of hydrogen at the time of saturation. The entry of spectra TSGR of hydrogen at thermo-stimulated discharge of gas was carried out with the help of a complex hardware-software, which enabled the controlling of the display of mass spectrometer MX-7304, to produce a linear heating of samples and recording in a file, the values of temperature and intensities of the selected lines of a mass spectrum (from 1 up to 6) with a speed from 1 till 10 measured/s. Final treatment of experimental data was produced with the help of a package of applied programs OriginPro 7.0 (OriginLab computation). More details about the procedure of measuring and analysis are given in Ref. [4].

To estimate the hydrogen binding energy in traps we used the relations and calibration curves of the dependence of the desorption activation energy E_d on $T_{\max i}$ [5], where $T_{\max i}$ — the temperature at which the maxima in the hydrogen yield are observed at a certain linear heating rate (1 K/s in our experiments). Using the given relations and taking into account the small difference between binding energy of hydrogen atoms in the sample E_b and desorption activation energy E_d , it is possible (from the evident reason) to use the given relations for evaluating E_b .

3. Experimental results and discussion

During linear heating of samples, TSGR spectra of the following masses were observed: 1 amu (H), 2 amu (H_2), 3 amu (DH), 4 amu (D_2), 13 amu (CN), and 17 amu (OH). The D_2 mass was traced only after saturation with heavy water. TSGR spectral shapes for H, H_2 , DH, and D_2 masses were identical; the differences for masses CH and OH consisted in peak positions at lower temperatures. A comparison of the intensities of the above masses after saturation in electrolytes based on heavy and ordinary water showed that the most intense mass over the entire TSGR is OH in both cases. The difference is that the DH and D_2 masses appear in the spectra after saturation in the electrolyte based on heavy water; their total intensity (over the TSGR spectrum) is lower than that of OH and H_2 by a factor of 2–3. The results only on the H_2 yield are presented here, since there is no reason to consider that this will somehow affect the reliability of conclusions.

The modification of a hydrogen H_2 TSGR spectrum from a saturation time of 12Kh12M1BFR samples is shown in Fig. 1. Appreciable spectrum with a maximum at $T \approx 500^\circ\text{C}$ (hydrogen binding energy $E_b \approx 1.5$ eV/atom) appears after 12 h of saturation. This peak disappears, and hydrogen peak at $\approx 500\text{--}600^\circ\text{C}$ appears after 24 h saturation time (the binding energy in traps is $E_b \approx 1.5\text{--}1.7$ eV/at.). When the saturation time becomes more than 24 h, this peak moves to the area of $400\text{--}500^\circ\text{C}$ and broadens. At a saturation time of 48 h (curve 4), the peak intensity in the range of $400\text{--}500^\circ\text{C}$ ($E_b \approx 1.2\text{--}1.5$ eV/at.) increases and a peak near 900°C ($E_b \approx 2.4\text{--}2.6$ eV/at.) appears.

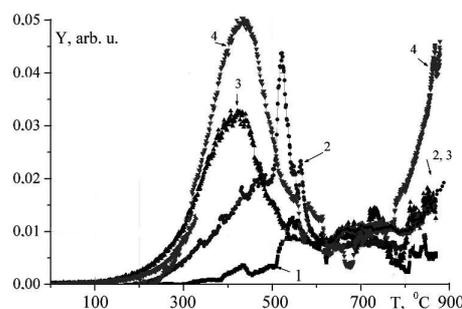


Fig. 1. Hydrogen TSGR spectra for 12Kh12M1BFR steel samples at various saturation times (h): 1 — initial sample, 2 — 12, 3 — 24 and 4 — 48 h. The saturation current density is 0.5 A/cm²; the electrolyte is 1 M H_2SO_4 .

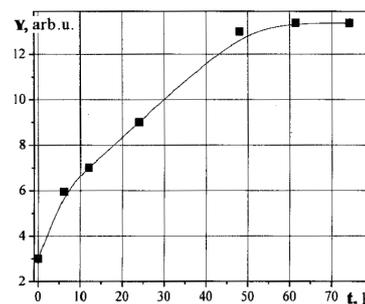


Fig. 2. Dependence of integral yield of hydrogen H_2 from saturation time according to integration of spectra of Fig. 1.

At the further increases of saturation time (64 and 72 h, Fig. 2), the general shape of the spectrum and the total intensity of the peaks shown in Fig. 1 remain unchanged; only relative fluctuations in their intensities occur, which is probably caused by the sample preparation procedure. In general, the described features are characteristic for all types of studied stainless steels; insignificant differences consist in the values of E_b and saturation times. It gives evidence that the mode of processing samples before saturation prevails over the influence on samples under the action of an electrolyte during saturation. The indicated behavior of spectral maxima of TSDE H_2 depending on saturation time specifies, on the one hand, the change of hydrogen binding energy in metal, and on the other hand the appearance of high temperature traps in samples during saturation after 48 h. It is confirmed by secondary ions mass-spectrometry method [6]; hydrogen implanted at electrochemical saturation is layered proportionally extremely non-uniformly on the depth of sample: its concentration increased near the surface layer. Therefore the appearance of high-temperature traps is logic for connecting with penetration of hydrogen at long times of saturation in volume of a sample.

Figure 2 shows the result of integration TSGR of hydrogen (Fig. 1) at different times of saturation. From

Fig. 2 it is clear that the relation $Y(t)$ is practically linear up to ≈ 50 h of saturation time. Then $Y(t)$ is stationary at time greater than 50 h. Except for that, it is clear that the total of the maximum emission is 6 to 7 times higher than the emission from the initial sample (for Pd, Ti and Zr analogous relation may be of the order of 3–5).

Data of Fig. 1 and Fig. 2 can be explained both by large hydrogen content in initial samples, which is not deleted by the annealing during preparation procedure of samples, and by small concentration of high-temperature traps in which hydrogen is captured during long time of saturation. It is interesting to note that at equal conditions of the electrolytic saturation the hydrogen absorption for 5 min in palladium is 4 orders greater than in steel for 72 h.

The 12Kh12M1BFR samples after 48 h of saturation were irradiated by X-rays with energy 120 keV for one hour under the conditions of atmosphere. The effects of such irradiation on the spectrum at the temperature range of 400–500°C is not observed, at the same time; at the temperature range of 800–900°C there is tendency to insignificant decrease. This can be interpreted as the absence of an appreciable effect of X-ray radiation on filling of surface hydrogen traps and partial hydrogen release from bulk traps.

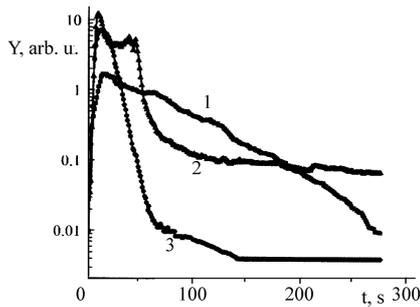


Fig. 3. Dependences of intensity of hydrogen releases from palladium on the electron irradiation time at different current densities. Electron energy $E = 40$ keV, J ($\mu\text{A cm}^{-2}$): 1 — 3, 2 — 15, 3 — 30. The maximal temperatures of samples under electrons beam ($^{\circ}\text{C}$): 1 — 30, 2 — 70, 3 — 250.

Figure 3 shows the dependences of the hydrogen yield from palladium on irradiation time at different current densities of electrons.

Figure 4 shows the dependences of the hydrogen yield from 12Kh12M1BFR steel on irradiation time at different current densities of electrons.

A comparison of Figs. 3 and 4 shows the following general feature and differences in the presented dependences.

First, a qualitatively identical yield variation with the irradiation time is observed for both palladium and steels as the current density increases, i.e., the maximum yield increases and shifts to smaller times with the increase of current density. The difference consists in the dynamic range of hydrogen yield (more than four orders of magnitude for palladium and slightly more than one order

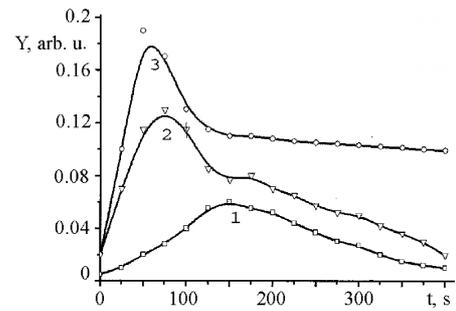


Fig. 4. Dependence of intensity of hydrogen releases from 12Kh12M1BFR stainless steel from electron irradiation time at different current density. Electron energy $E = 40$ keV J ($\mu\text{A cm}^{-2}$): 1 — 3, 2 — 15, 3 — 30. The maximal temperature of samples under a beam ($^{\circ}\text{C}$): 1 — 30, 2 — 50, 3 — 200.

of magnitude for stainless steel, despite the fact that the electron current density for palladium was the same as for stainless steel). The significant heating of samples to 70–150°C (curves 3 in Figs. 3 and 4) in case of a palladium induce the structure of the curves with two maxima in the curve vertex region (Fig. 3). The intensity ratio of these maxima may be different. It is reasonable to explain this structure at least in terms of two mechanisms of radiation-stimulated hydrogen release associated with electron and temperature exposure. Let us note that this structure is observed only in the case of palladium and is not observed for steels. This corresponds to the peak positions in TSGR H_2 spectra of palladium and stainless steels (about 200°C for Pd and 400–500°C for stainless steel (Fig. 2)).

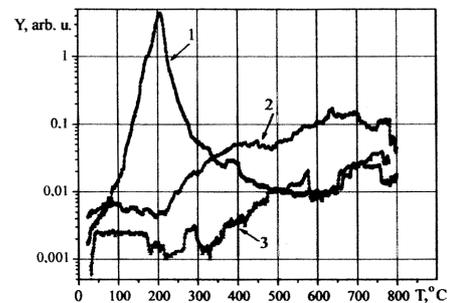


Fig. 5. TSGR spectra before (1) and after (2, 3) electron irradiation of hydrogen charged palladium: 1 — initial hydrogen charged sample; 2 — irradiated with current density $J = 3 \mu\text{A/cm}^2$, $t = 10$ min; $T_{\text{irr}} = 30^{\circ}\text{C}$, 3 — irradiated: $J = 30 \mu\text{A/cm}^2$, $t = 10$ min, $T_{\text{irr}} = 250^{\circ}\text{C}$.

Figure 5 shows the TSGR spectra before and after electron irradiation of the hydrogen charged palladium samples. The amount of the got out hydrogen (in percentages) as a result of irradiation can be obtained if these curves are integrated and the ratio $(I_{\text{ini}} - I_{\text{irr}})/I_{\text{ini}}$ is taken (where I_{ini} and I_{irr} — magnitudes of integrals before and after irradiation, accordingly). It was obtained in such a

way: the maximum quantity of hydrogen which can be removed for 1 h with $30 \mu\text{A}/\text{cm}^2$ current density — 90% from palladium and only 60% from stainless steel.

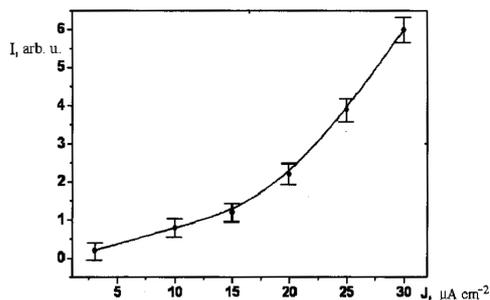


Fig. 6. Dependences of integrated hydrogen release from steel according to integration of curves in Fig. 4.

The dependence of the total (over the spectrum) hydrogen yield on the electron current density (for steel — Fig. 6, for palladium [7]) for steels appears to be similar to the same dependence for palladium.

Experimental points in the dependences are well approximated by the formulae

$$Y = A \exp(J/B) + C, \quad (1)$$

where Y is the total yield; J is the electron current density; and A , B , and C are constants. The dependence of Y on J for steels is also obviously nonlinear, as for palladium [7]. It follows from Eq. (1) that $BdY = (Y - C)dJ$, i.e., the increment of the molecular hydrogen yield dY is proportional to the increment of the electron beam current density dJ and the molecular hydrogen content in the surface region. This is probably caused by that the electron beam in the surface region promotes H^+ ion neutralization and heterogeneous recombination of H atoms into H_2 molecules followed by molecular hydrogen desorption.

4. Conclusion

The obtained results lead to the following conclusions.

For 12Kh12M1BFR steel for times of saturations (in electrolyte — 1 M H_2SO_4 , current density — 0.5 A cm^{-2}) less than 50 h the amount of introduced hydrogen linearly grows with saturation time, and the temperature spectrum TSDR H_2 changed the position, under these changes spectrum may be interpreted as follows. In the beginning there is a capture of hydrogen at the low-temperature ($400\text{--}500^\circ\text{C}$) traps of several types, located at the surface (hydrogen binding energy on traps $E_b \approx 1.2\text{--}1.5 \text{ eV/atom}$). And only at times of saturation of 48 h and more hydrogen penetrates to high-temperature ($800\text{--}900^\circ\text{C}$) to the traps which located more deeply under the surface layers (hydrogen binding energy on traps $E_b \approx 2.4\text{--}2.6 \text{ eV/atom}$).

Under electron bombardment, the most intense release of hydrogen from the palladium and other prime metals is observed over the first two minutes. The intensity reaches

its maximum depending on a electron current density; at a current density $\approx 30 \mu\text{A cm}^{-2}$ intensity reaches its maximum within 5–50 s (for different metals) after the onset of bombardment.

A nonlinear increase in the hydrogen yield with the electron beam current density and energy during irradiation of sample is most probably caused by electronic processes (Auger emission, core atom ionization, and plasmon excitation) involved in hydrogen diffusion and desorption activation.

Experiments have shown also that at electron energy 40 keV with current density $J = 30 \mu\text{A cm}^{-2}$ the samples are heated to a temperature of $\approx 250^\circ\text{C}$. In this way 90% of hydrogen escapes from palladium and 60% — from steel within 1 hour of an irradiation. It is necessary to increase the energy of electrons to the range of 40–100 keV and decrease the electron current density for the more effective removal of hydrogen without increase of temperature.

Under the action of electrons and X-ray quanta with energy of 40 keV, hydrogen leaves mainly the low-bond energy traps; under the action of X-ray quanta with energy of 120 keV, hydrogen is removed from traps of all types.

The efficiency of hydrogen removal from metals and alloys subjected to ionizing radiation substantially depends on the chemical composition and structure of alloys and, simultaneously, on the type, energy, and density of radiation.

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References

- [1] Z. Chuanxiang, L. Shaohui, *Int. J. Hydrogen Energy* **32**, 3508 (2007).
- [2] H. Baumbah, M. Kroning, Yu.I. Tyurin, I.P. Chernov, Yu.P. Cherdantzev, *Nonequilibrium Systems Metal–Hydrogen Titanium, Ferrite Steel*, Publ. House of Tomsk University, Tomsk 2002, p. 350 (in Russian).
- [3] V.G. Gavrilyuk, V.N. Shivanyuk, J. Foct, *Acta Mater.* **51**, 1293 (2003).
- [4] N.N. Nikitenkov, A.M. Khashkhash, I.A. Shulepov, V.D. Khoruzhii, Yu.I. Tyurin, I.P. Chernov, E.N. Kudryavtseva, *Instrum. Exp. Techniq.* **52**, 865 (2009).
- [5] D.P. Woodruff, T.A. Delchar, *Modern Techniques of Surface Science*, Cambridge Univ. Press, New York 1986.
- [6] N.N. Nikitenkov, D.Yu. Kolokolov, I.P. Chernov, Yu.I. Tyurin, *Vacuum* **81**, 202 (2006).
- [7] N.N. Nikitenkov, Yu.I. Tyurin, I.P. Chernov, A.M. Lider, A.V. Skirnevskii, *J. Surf. Investig. X-ray Synchrotron Neutron Techniq.* **2**, 440 (2008).