Radiation-enhanced Hydrogen Yield from Palladium

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Abstract – Singlet and molecular hydrogen yield from palladium at electron irradiation with energy 40 keV at current densities from 10 up to 100 μA/cm^2 was investigated with mass-spectrometer methods. Hydrogen charging in palladium samples was carried out with electrolytic expedient. The hydrogen concentration in samples before and after irradiation was checked by gas thermo-desorbtion method. The peak of hydrogen intensity is attained within the first 5–15 seconds after the beginning of irradiation. The maximal hydrogen yield from samples is observed during first 1–3 minutes. Thus at small current densities the temperature of the sample was incremented no more, than up to 30 ^{0}C, at major – up to 250 ^{0}C. There appeared more than 90 % of hydrogen leaves from samples at irradiation by high current densities. The stayed hydrogen is captured on traps which have not been observed before electron irradiation.

1. Introduction

Palladium has the highest miscibility of hydrogen from all known materials and it is one of the best catalytic agents. Therefore it calls major interest in connection with problems of hydrogen energetics, in particular, makings of fuel cells.

Hydrogen can be present at metals with major concentrations in flaws of all types and to define the mechanical, electrical and radiative properties of materials [1]. Therefore the study of hydrogen behaviour at it charging in metals and radiation-actions has especially important value for problems of a materials technology. Earlier [1–5], some reliable results on a hydrogen atoms motion and the isotopic effects have been received during hydrogen charging and an electronic irradiation of titanium, stainless steel and palladium samples.

The present article is prolongation of the indicated works.

2. Experimental technique

Singlet and molecular hydrogen yield from palladium at electron irradiation researched by mass-spectrometer methods. The hydrogen content in samples before and after an irradiation was checked by gas thermo-desorbtion method (GTDM). Equipment for GTDM research described in [1]. The cell for a heating of samples conjugate with mass-spectrometer through the gateway. In a measuring cell of a mass spectrometer the pressure is not worse 10^{-5} Pa. Without oil finishing pump-down was carried out a magnet-discharge pumps. For recording of mass-spectrums and for tracking of intensities of separate spectral lines used the spectrometer MX-7304 with sensitivity elements and molecules of a residual atmosphere in a vacuum chamber ~10^{-8} Pa.

For controlling a sample heating and tracking of mass lines intensity was used a special automatization system on the basis of a personal computer. The system allows to trace simultaneously and continuously from 1 up to 6 masses (any of a mass spectrum), gases oozed from a sample during an electron irradiation or a heating.

The step of measurings thus can vary from 1 up to 100 points in a second.Thus the linear heating of samples from 20 up to 1100 °C can be make with velocity from 0.1 up to 5 degree/c. The relative accuracy of measuring for intensity of a mass spectrum lines does not exceed 5 %.

The hydrogen charging in a samples of palladium was carried out the electrolytic expedient at a current density of electrolysis J=0,5 A/cm^2 during 6 minutes. The palladium foil with the area ~2 cm^2 and thickness d~100 μm used as a samples of palladium.

The electronic gun with energy up to 100 кэВ and currents from 1 up to 200 мкА has been used for irradiation of palladium samples.

The samples temperature T_{irr} during an irradiation was checked by the thermoelectric couple on a surface of a sample inverse irradiated. All experiments are made on the same two equal samples of a foil which were charged by hydrogen, irradiated and annealed multiply.

Dependences of hydrogen yield on irradiation time and on temperature are investigated.

3. Results and discussion

Fig. 1 shows intensities of 4 spectral lines of hydrogenous masses traced at thermo-desorbtion from Pd samples defore (a) and after (b) electrons irradiation. Intensity in zero corresponds vacuum level of intensity (prior to the beginning of a heating). From comparison Figs. 1 a and b would be visible that intensity of lines OH^+ and CH^+ in thermo-desorbtion spectra as a result of electron irradiation varies not considerably. At the same time the thermo-desorbtion spectra H^+ and H_2^+ varies considerably: before irradiation the maximum in these spectra is observed at T~200 °C, after irradiation at T~600 °C; intensity of H^+ and H_2^+ varies within 4 orders. These regularities testify, that spectrum lines OH^+ и CH^+ are stipulated (in basic) by a residual atmosphere in a vacuum chamber while

OH^+ and CH^+ release from palladium samples. In Fig. 2 the thermo-desorbtion spectra H_2 before and after an electrons irradiation of palladium samples with different beam current density are compare. It is visible, that the increasing of a electrons current density essentially reduces quantity of the hydrogen remaining in samples: the relationship between areas under curves 1–3 (Fig. 2) S_1:S_2:S_3 is equal 1:0.23:0.04. Let's note, that the spectrum 3 practically does not vary at a recycle of a heating without hydrogen charging sample, that is corresponds to initial.

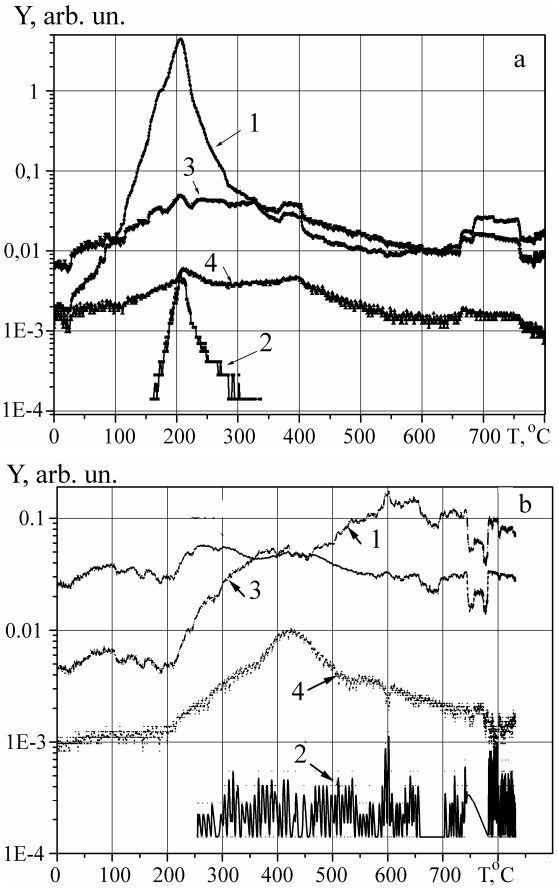

Fig. 1. The thermo-desorbtion spectra of the basic hydrogenous molecules from palladium before (a) and after (b) electron irradiation: 1 – H_2, 2 – H, 3 – CH, 4 – OH. Requirements of an irradiation: J=10 μA/cm^2, t=10 min; T_{irr} = 30 °C

Fig. 2 shows also, that at transition from initial to irradiated samples disproportionation of intensity in spectrums occurs: from initial samples the maximum of hydrogen yield is observed at T~200 °C, after an irradiation – at T~600 °C. Thus intensity of H_2 yield at T>600 °C from irradiated sample above than from initial. It is possible to explain by removal of hydrogen (during an irradiation) from traps with a loose coupling in vacuum and entrapment of small amount of hydrogen on traps with the close coupling, which are generated during an irradiation.

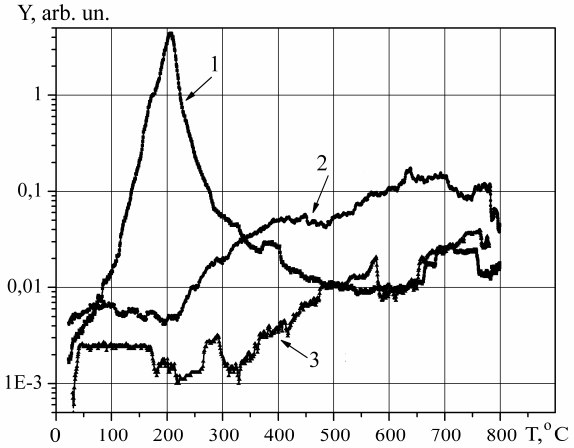

Fig. 2. The thermo-desorbtion spectra before (1) and after (2, 3) electron irradiation hydrogen charged palladium: 1 – initial hydrogen charged sample; 2 – irradiated with current density J=3 μA/cm^2, t=10 min; T_{irr} = 30 °C, 3 – irradiated J= 30 μA/cm^2, t=10 min, T_{irr} = 250 °C

Fig. 3 shows the dependences of intensity hydrogen yield H_2 on three current densities of electron beam. It is visible, that intensity in a maximum and the shape of the curves strongly depend on current density. At increasing of a current density occurs decreases of the rise time and wane time of intensity. So, the maximum of a curve 1 is attained through 14 s, a curve 2 – through 11 s, 3 – through 9 s. At the current densities, resulting to the considerable heating samples in a vertex part of curves the structure is observed with two and more maxima (curve 3), and the relation of intensities in these maxima can be variously. This structure may be explain by presence as a minimum of 2 mechanisms for radiation-enhanced hydrogen yield, one of which is stipulated by action of electrons, another – by temperatures.

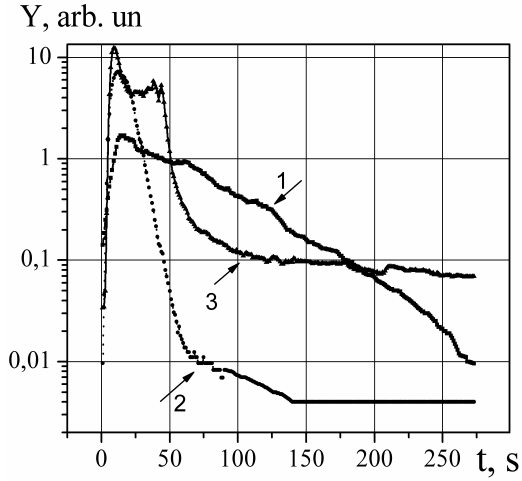

Fig. 3. Dependences of hydrogen yield from palladium on irradiation time at different current densities of electrons. J (μA·cm^{-2}): 1–3, 2–15, 3–30.
The peak temperature of samples under electrons beam (°C): 1 – 30, 2 – 70, 3 –250

Fig. 4 shows dependence of an integrated hydrogen yield on electrons current density according to our experiments. The experimental points are approximated by a curve shown on this figure:

$$Y = A \cdot \exp\left(J/B\right) + C, \qquad (1)$$

where A=0.29, B=4.74, C=113.29.

From (1) follows: $BdY=(Y-C)dJ$. Thus, the increase of molecular hydrogen yield is proportionally to increase of a current density of electron beam J and quantity of molecular hydrogen Y in near-surface areas. It probably testifies that the electronic beam ensures neutralization of H^+ ions and boosts a heterogeneous recombination of atoms H in molecules H_2 with the subsequent desorption of molecular hydrogen.

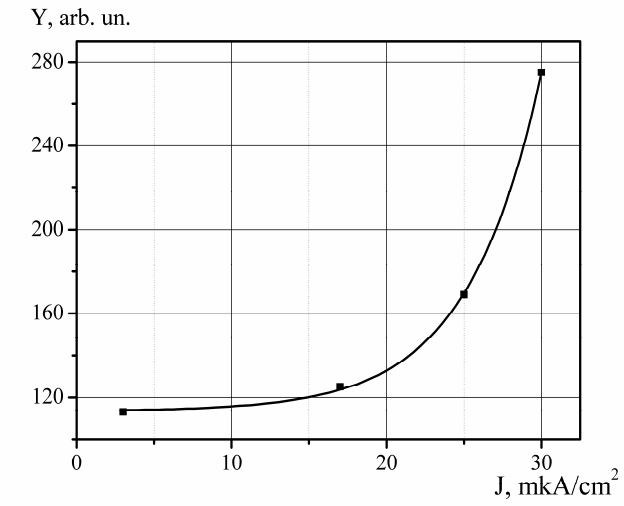

Fig. 4. Dependence of an integrated hydrogen yield from palladium on electrons current density. Irradiation time – 10 minutes.
Electrons energy – 40 кэВ

The received results demand for their explanation of the inclusion several mechanisms of a hydrogen yield. In blanket the process is represented as follows. During electron irradiation in a near-surface layer (thickness ~ electrons run) forms surplus of an electron concentration and a deficiency of protons (nucleus of hydrogen) concentration. It stipulates making in a sample of lapse rates electrostatic, magnetic and temperature fields (besides concentration gradients). These lapse rates initiate various diffusion streams which diffusion constants can be much higher than thermal. Electron irradiation besides removes the surface potential hill for yield of atoms from a sample.

4. Conclusion

Under requirements of an irradiation indicated in the present work the following basic regularities of hydrogen yield from palladium are observed:

1. A maximum the hydrogen yield is attained within the first of 5–15 seconds.
2. The maximal hydrogen yield is observed during first of 1–2 minutes.
3. The temperature of a sample can be incremented more, than up to 250 ^oC at current densities up to 50 мкА/sm^2.
4. At thermo- enhanced eduction the maximum of hydrogen yield is observed at T~250 ^oC before electron irradiation and at ~600 ^oC after an irradiation.
5. As a result of electron irradiation at current densities of ~30 мкА/cm^2 and are higher from samples leaves more than 90 % of hydrogen. The stayed hydrogen is captured on traps which is not observed before electron irradiation.
6. Dependence of an integrated hydrogen yield on electrons current density of is not linear.

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