Radiation-induced hydrogen transfer in metals

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Abstract. The paper presents processes of hydrogen (deuterium) diffusion and release from hydrogen-saturated condensed matters in atomic, molecular and ionized states under the influence of the electron beam and X-ray radiation in the pre-threshold region. The dependence is described between the hydrogen isotope release intensity and the current density and the electron beam energy affecting sample, hydrogen concentration in the material volume and time of radiation exposure to the sample. The energy distribution of the emitted positive ions of hydrogen isotopes is investigated herein. Mechanisms of radiation-induced hydrogen transfer in condensed matters are suggested.

Keywords: hydrogen, condensed matter, radiation-induced transfer, non-equilibrium release, plasma

1. Introduction

The hydrogen behavior in metals is the important scientific and technical problem for a wide range of basic and applied research. The problem of hydrogen permeability and accumulation is interesting due to the need for new construction materials for nuclear, thermonuclear and hydrogen power engineering and solutions of materials science problems [1-7]. It was found that the radiation exposure and control for hydrogen concentration in the bulk of solids provide creation of non-equilibrium thermodynamic systems, the synthesis of which is not possible to achieve using traditional methods [8-13].

Complex experimental and theoretical studies were performed to understand the behavior of hydrogen in metal-hydrogen systems exposed to ionizing radiation (X-rays, electrons with energies below 100 keV).

The obtained results indicate [5,14-18] that hydrogen isotopes taking regular positions in metal, form its own hydrogen subsystem. Energy introduced during the radiation exposure is accumulated by the hydrogen subsystem and hydrogen isotope atoms acquire energy greater than that of the metal matrix for the time period much longer than at electron-phonon relaxation. Hydrogen isotope movement stimulates the diffusion of impurity atoms and leads to restructuring of the metal defect structure. The unique accumulating properties of hydrogen subsystem in metals are described by the following experimental facts:

- Radiation-induced hydrogen yield from metals at room temperature or below;
- Superlinear hydrogen yield rate from metals depending on the concentration of injected hydrogen and radiation intensity;
- A non-equilibrium desorption of H and D atoms and H^+ and D^+ ions from the metal surface saturated by hydrogen at electron beam exposure;

- Removal of hydrogen from the total metal volume in irradiating a local surface area.

2. Experimental

2.1. Methods of mass-spectrometric analysis of desorption from hydrogenated metals and non-equilibrium migration of deuterium through metals. In situ investigations.

The design of the installation is shown in Figure 1. The installation [5,14] (Figure 1) allows performing electrolytic saturation of metal samples with hydrogen (deuterium), monitoring hydrogen (deuterium) migration through metal and hydrogen (deuterium) yield in vacuum. The yield of H, D atoms is stimulated by accelerated electrons (E = 1 - 100 keV, j_e = 1 – 150 mA/cm^2) or X-ray radiation (E_x = 1.0 – 100 keV, $j_x = 10^{13} – 10^{15}$ photons / (cm^2·s)). Recording of H and D atoms is carried out by time-of-flight mass-spectrometer. The samples are presented by Pd with 0,1 mm thickness; Ti with 0,05 mm thickness; Nb with 0,1 mm thickness. The electron beam is directed from the gun and focused on the saturating sample or converted into the X-ray beam after a tungsten plate passing. This installation allows mass spectrometric measurements of metal deuterium yield rate when exposed to the electron beam during the linear heating.

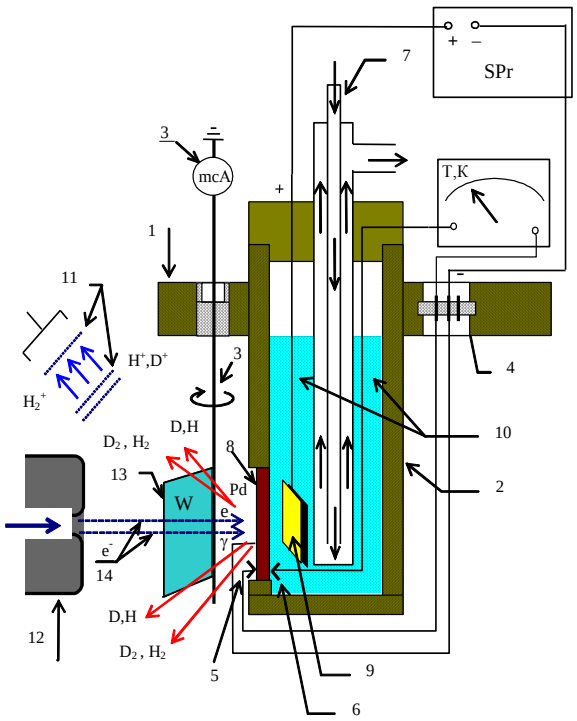


Figure 1. Schematic view of the cell for in situ studying non-equilibrium migration of hydrogen and deuterium in metals: 1 - flange; 2 - electrolysis glass; 3 - measuring device for electron beam and X-ray generation; 4 - vacuum current leads; 5, 6 - thermocouples; 7 - flow refrigerator; 8 - sample; 9 -platinum electrode; 10 - electrolyte; 11 - mass spectrometer; 12 - electron gun; 13 - tungsten foil; 14 - electron beam; 15 - cell power supply

2.2. Method for studying non-equilibrium yields of atomic hydrogen from metals under irradiation

Having a high sensitivity, the mass-spectrometric technique, recoil nucleus method does not answer the fundamental questions: whether hydrogen at the local irradiation exposure yields form the entire surface of the sample or from the point of the beam impact. The hydrogen atom yield from the metals is observed using the phenomena of heterogeneous chemiluminescence [15] and the bleaching effect of some kinds of organic dyes applied to a catalytic substrate [16]. In order to avoid effects associated with X-ray and cathodoluminescent glow, a method of H, D atoms visualization was chosen using the appropriate dyes.

2.3. Deuterium migration and yield under electron and X-ray radiation

Study of migration, diffusion, and hydrogen isotope release from metals under the action of accelerated electrons and X-ray radiation was carried out on stainless steel, niobium and palladium samples. These materials substantially differ in hydrogen isotope solubility. The minimum solubility is in stainless steel, the maximum - in palladium. Fig. 2a shows the yield rates of deuterium ($I_D cm^{-2} s^{-1}$) from stainless steel under the electron beam exposure. In these measurements, the temperature of the outer sample side in the electron beam area is not over 60 ° C, while on the back side – 40 °C. At these temperatures, in absence of the electron beam, the equilibrium deuterium yield is insignificant. The most pronounced effect from radiation-induced deuterium release under the electron beam exposure is in palladium (Figure. 2b).

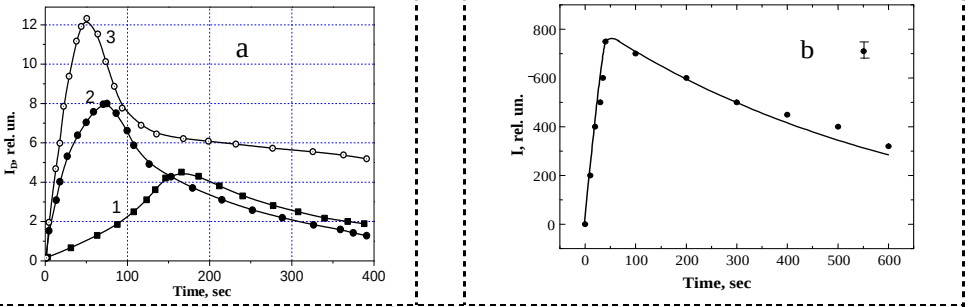


Figure 2. (a) Deuterium ($I_D cm^{-2} s^{-1}$) yield rate from stainless steel under the irradiation. Electron energy E = 20 keV, current density: j, mA/cm^2: 1 – j_1 = 250, 2 – j_2 = 500, 3 – j_3 = 750.
(b) the intensity of deuterium yield from Pd under electron beam (T = 40 °C, E = 20 keV), the current density j = 100 mA/cm^2

The rate of deuterium realese from metals under electron beam superlinearly increases with increasing the beam current and injected deuterium concentration.

The superlinear dependence indicates unequivocally the collective processes in the metal-hydrogen system under ionizing radiation.

The flow chart of experiment on atomic hydrogen release from PdDx is shown in Fig. 3 [17,18]. The electron beam with energy of 20 keV, diameter of 3 mm formed with copper (thickness t = 0.1 cm) and iron diaphragms (t = 0,4 cm) is directed to 15 x 10 mm palladium sample with thickness of 60 μm electrolytically saturated with deuterium. The 20 keV electron run in Pd is 1 μm or 60 times less than the thickness of the sample. Except for the electron beam formation, diaphragms performed the function of attenuation of bremsstrahlung radiation produced by the electron gun. Dyes were placed above and below the sample. In order to observe the intensity distribution of atom release along the surface, the additional copper plate with holes was placed between Pd and dye (Fig. 3). The whole "sandwich" consisting of the top, bottom dyes, palladium and copper plate is compacted to eliminate lateral gaps between them.

Under the influence of the electron beam, dye bleaching is observed (Fig. 4a) indicating the atomic deuterium yield both on the beam side (Fig. 4b) and the reverse side of the sample (Fig. 4c) not directly irradiated by electrons. Thus, electrons that have the run in the metal are much lower than its thickness, can excite the deuterium (hydrogen) subsystem in the whole volume of the sample.

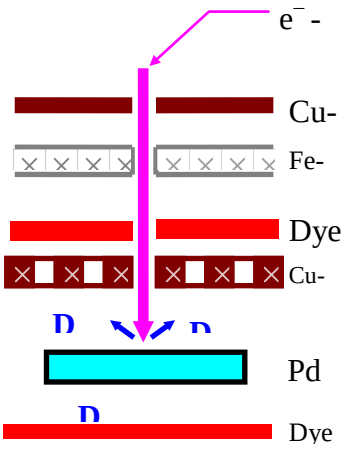


Figure 3. The flow chart of experiment on atomic hydrogen release from PdDx induced by 20 keV electron beam energy

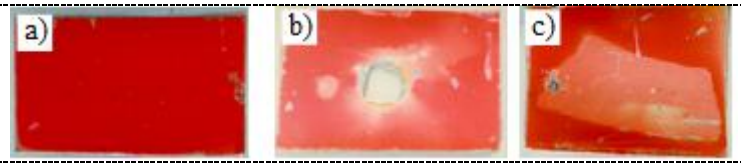


Figure 4. Deuterium PdDx release under 20 keV electron beam energy, a - original dye; b - upper dye; c - lower dye

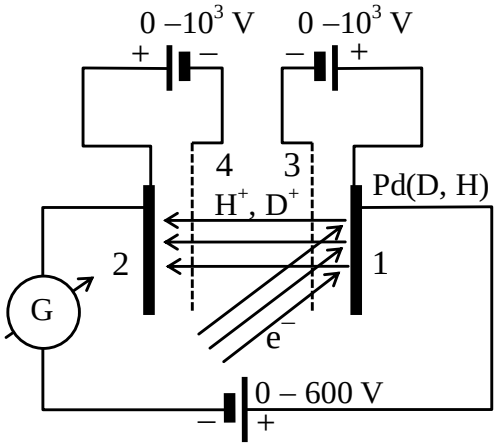
2.4. Emission of positive ions under Pd irradiation saturated by hydrogen and deuterium

Radiation by metal electrons saturated by hydrogen (deuterium) stimulates the non-equilibrium yield from Pd (D, H), Nb (D, H) of not only H_2, DH, D_2 molecules [16], but also free H, D atoms [5,16,18]. Since even the thermally equilibrium heating of metals with the adsorption layer is accompanied by the emission of positive ions, it is expected that the metal supply with the saturated by hydrogen (deuterium) radiation energy will lead to the excitation of the internal hydrogen atmosphere and can induce the non-equilibrium emission of positive ions from the metal surface. The cell with a sensor was additionally placed in the installation (Fig.5a) to record positive ions (Fig.5b). The electron beam current could vary from 1 to 100 uA, and beam energy from 0.1 to 100 keV.

A significant degree of non-equilibrium in the hydrogenous (deuterium) palladium subsystem ($\hbar\omega/kT \cong 10$ at 313 K) can cause not only the yield of free atoms from Pd surface, but also the emission of positive ions (H +, D +) under electron irradiation.

In irradiating Pd by the electron beam with 50 keV energy and I_e =2–10 uA current the emission of positive ions was detected with the maximum current of 0.2 uA at beam current of 10 mA (0,1 at 6 uA, 0.04 at 4 uA and 0.012 at 2 uA). The emission current of positive ions decreases with the removal of hydrogen (deuterium) from Pd (Fig. 5 (b), curves 4, 5). Curves 2, 5 shown in Figure 5 (b) were obtained at interval corresponding to the passage through the cathode charge ~ 10^{-2} Kl (~ $6{\cdot}10^{16}$ electrons, $\Delta t = 10^4$ s). The increase in the emission of positive ion current correlates with the intensity increase of hydrogen and deuterium bands in mass spectra.

Small emission current of positive ions is observed at irradiating Pd (D, H) by γ-rays. An interesting feature of obtained results is the quadratic increase in the emission current of positive ions from the electron beam current. A good approximation of this relationship is the formula (I^+ and I_e in uA): $I^+ = 2.7{\cdot}10^{-3} I_e^2$.



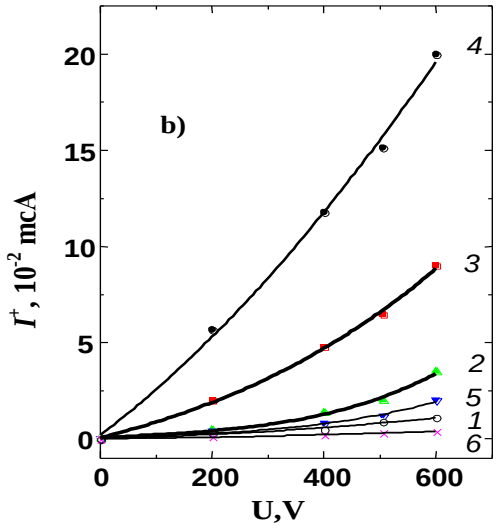


Figure 5. a) a schematic diagram of the cell for rerecording positive ions releasing from the Pd (D, H) under electron beam radiation: 1 - irradiated Pd (D, H) 'cathode'; 2 - anode collecting (protons); 3, 4 - grids locking (electrons). b) current-voltage characteristics of ion Pd (D, H) emitter irradiated by electrons. Electron beam currents: 1 - 2 mkA; 2 - 4 mkA; 3 - 6 mkA; 4 - 9 mkA; 5 - 4 mkA (irradiation at lower D and H concentrations in Pd as compared to (2)); 6 - X-ray irradiation of Pd (D, H).

The nonlinear increase in the emission current of positive ions from the electron beam is typical for processes involving the excited hydrogen atmosphere of metals. Excitation of the hydrogen atmosphere in metal results in the increase of H, D atom amount yielded from the metal onto the surface and the number of positive ions removed from the surface. A combination of these factors leads to a non-linear increase of the emission current of positive ions from the electron beam current.

The dependences between the positive ion current and the energy of accelerated electrons and between the ion distribution and the energy of the electron beam are shown in Figure 6. The positive ion current decreases with decrease of the accelerated electron energy within 6 keV region that is not associated with the decrease of power supplied to Pd (D, H) electron beams. In the experiment, the power supply $I_e E$ = 0.3 W is constant - beam current increases with the decrease of the electron beam energy.

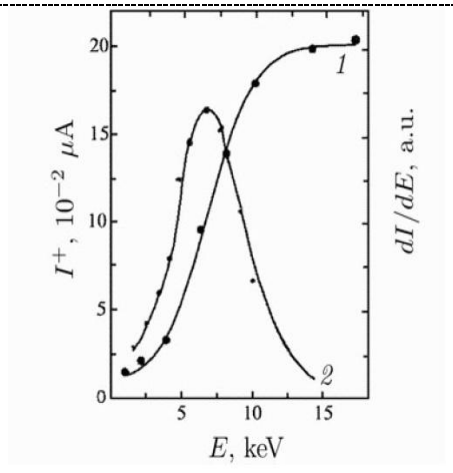


Figure 6. Dependences between the positive ion current and the energy of accelerated electrons (1) and the ion distribution and the energy of the electron beam (2). The power supply of Pd(D, H) ($I_e E$ = 0.3 W) is constant.

6. Conclusion

A study of the hydrogen behavior in metals under ionizing radiation shows:

- Hydrogen in metals forms its own subsystem;
- Hydrogen subsystem in metals transforms to the excited state during the exposure to ionizing radiation;
- Migrating hydrogen provides the defect and impurity atom diffusion and organizes the metal structure.

A mechanism of non-equilibrium hydrogen yield and its isotopes from metals is connected with the specific accumulative properties of hydrogen in metals. Given that the degree of Pd saturation with hydrogen is high and corresponds approximately to one H (D) atom per Pd atom, then the energy of plasma oscillations in the hydrogen subsystem Pd:

$$\hbar\omega = \hbar e\sqrt{\frac{\rho_{Pd} N_A}{M_{Pd} m_p \varepsilon_0}} \cong 0.2eV\,, \qquad (1)$$

where ρ_{Pd}, M_{Pd} are the density and molar mass of palladium respectively; m_p is the mass of a proton; N_A is the Avogadro's number; ε_0 is the dielectric constant; e is the elementary charge.

The value of the non-equilibrium oscillation energy can be obtained from a comparison of the effective and equilibrium diffusion coefficients of hydrogen in Pd.

The applied nature of the observed phenomenon is as follows:

- the development of methods of low-temperature hydrogen removal from construction materials and recovering their mechanical properties;
- dosed hydrogen extraction from the hydrogen storages (hydrogen energetics);
- radiation technologies of hydrogen brittleness prevention.

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