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COMPARATIVE ANALYSIS OF DEUTERIUM IONS IMPLANTED AND DEUTERIUM ATOMS SATURATED AT HIGH PRESSURE IN PURE Pd AND Pd DILUTED ALLOYS

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Pd and its diluted alloys (Pd–Ag, Pd–Pt, Pd–Ru, Pd–Rh) were implanted by 25 keV deuterium ions at a fluence interval of $(1.2–2.3)\cdot10^{22}$ m^{-2}. The same property alloys were saturated by deuterium atoms using high pressure chamber during long period with temperature stabilization and electrical resistance measurement of standard Pd wire. The post-treatment depth distributions of deuterium and accompanied hydrogen atoms were measured immediately after implantation (ten days) and after definite time period (three months) after saturation with the usage of elastic recoil detection analysis (ERDA). After two months, the measurements were repeated. The comparison of obtained results in both series of studies allowed one to make an important observation of a relative stability of deuterium and hydrogen atoms in pure Pd and its diluted alloys.

В Pd и его разбавленные сплавы (Pd–Ag, Pd–Pt, Pd–Ru, Pd–Rh) были имплантированы ионы дейтерия с энергией 25 кэВ в интервале флюенсов $(1,2–2,3)\cdot10^{22}$ $м^{-2}$. Сплавы с теми же свойствами были насыщены атомами дейтерия в камере высокого давления в течение длительного времени при стабилизации температуры и измерении электрического сопротивления стандартного образца — Pd-проволоки. Исследования распределений атомов дейтерия и сопутствующего водорода по глубине были выполнены через 10 суток после имплантации-насыщения и по прошествии трех месяцев. Сравнение полученных в обеих сериях результатов позволило сделать вывод об относительной стабильности дейтерия и водорода в чистом Pd и его сплавах.

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INTRODUCTION

Limited energy resources and increasing pollution associated with energy production have stimulated the search for cleaner, cheaper, and more efficient technologies. One promising technology involves hydrogen stored in metal hydrides [1–4].

Hydrogen and its heavier isotopes serve as a nuclear fuel in fusion reactor power stations [5–9]. They are also utilized widely in currently operating nuclear reactors for slowing down of neutrons, but also as reflectors–mirrors of neutrons, as safety materials, and in the regulatory systems [7]. Besides that, there is a problem of creation of high neutron fluxes for various applications. The increasing of capacity of metal foils with deuterium near the surface is a very important problem, too. The basic challenge in all these applications and in the promising future ones, would be to obtain as high as possible concentration of hydrogen in storage-accumulators while creating relatively simple conditions for hydrogen desorption in hydrogen energetics [4–7] and possibly in future mobile-engine applications [2]. The increasing of deuterium atom concentration in some technological structures is an example of creation of high flux neutron sources

From the discovery of high permeability and saturation level of pure Pd by hydrogen (the 1888 year, see [7, 15]), the problem of detailed study of various its alloys, particularly with noble metals, takes great intention for purification of hydrogen gas and for its application as accumulator of hydrogen.

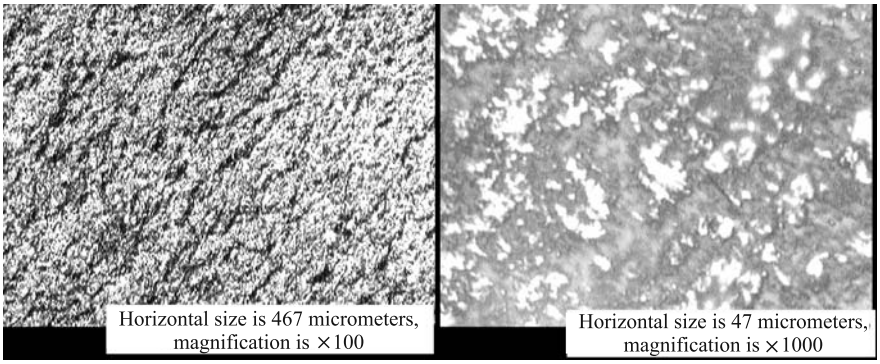
There is one good approach to measure, using some various methods (ERDA of course, too), the summary and depth concentrations of D and H atoms in Pd and its diluted alloys implanted up to high fluence of D^+ ions and saturated by D atoms at high pressure after long time of such treatment which gives one the possibilities to estimate the deuterium concentration by using radiation stimulating created traps.

The purpose of this report is a study of depth distributions of implanted deuterium ions in Pd, Pd-diluted alloys and some other materials; a research of its stability is another important concern of the study (see well-known reviews [8–13] and references therein); and then a comparison of hydrogen and deuterium depth and summary concentrations after long time saturation and after D^+-ion implantation into pure palladium and its diluted alloys.

1. EXPERIMENTAL METHODS AND SAMPLE PREPARATION

The Pd and Pd alloy single crystal ingots were grown at the Institute of Atomic Energy (Otwock/Świerk, Poland). Then some of these ingots were cut on thick plates with a thickness of $\sim 1-2$ mm. Then relatively thin foils were prepared by rolling, under pressure, these plates up to relatively thin films, and after mechanical and electrochemical polishing the final thickness of these foils was about 50–150 μm. The surface structures of Pd samples at two various magnifications ($\times 100$ and $\times 1000$) are presented in Fig. 1. It is seen that surface quality is mainly enough for the following studies taking into account also the smoothing of surface during D^+-ion implantation, too.

The first part of films was saturated by deuterium atoms in high-pressure deuterium chamber [14, 15], and the second part was implanted by D^+ions up to high fluences. The third and fourth parts of samples were annealed at temperature of about 900 K during 1 h and then were saturated (third part) and implanted up to the same ion fluences (fourth part).



a *b*

Fig. 1. The surface structures of initial Pd samples at two magnifications: ×100 (*a*) and ×1000 (*b*)

1.1. An Implantation of D^+ Ions at High Fluence Energy of 25 keV. The implantation of deuterium ions with the energy of 25 keV was carried out on special beam line of low-energy ion irradiation with a separation magnet, deviation systems in both vertical and horizontal directions, and a number of flux measuring Faraday's cups in both directions [16]. Homogeneity of irradiation on a square of about 6×4 cm was better than $\pm 5\%$. All samples were glued to cooling substrate, temperature of implantation was $\approx 30\,^{\circ}$C. It is necessary to note that the ion beam flux during implantation was about $35 \cdot 10^{17}$ $m^2 \cdot s^{-1}$, and ion beam power was less than 0.075 W/cm^2. All metal alloys were irradiated up to one ion fluence $1.2 \cdot 10^{22}$ m^{-2}. All implanted D^+-ion samples were checked with MOM and SEM for an absence of blistering and flaking. An atomic force microscope (AFM) was used for estimations of surface sputtering rates of all samples. The post-experimental metal surface roughness was comparable with computer code SRIM-2008 simulation of surface sputtering [17]. It is necessary to note that all implanted metal-samples were deformed by a spontaneous emergence of gas pores or gas bubbles (the so-called swelling processes). There was a surface discoloration with intensity depending on the D^+-ion implantation fluence.

1.2. Saturation of Pure Pd, Diluted Pd Alloys, Manganin ($Cu_{84}\,Mn_{14}\,Ni_2$) and Some Pure Metallic Samples (Zr, Ti, Cu) at High-Pressure Deuterium Setup [14, 15, 18, 19]. The time-dependent studies of deuterium and hydrogen atoms near the surfaces of some pure metals and alloys were started at the Institute of Chemical Physics of Polish Academy of Sciences (Warsaw, Poland). A special small-volume high-pressure deuterium/hydrogen chamber was used for long time saturation of various materials [14, 15, 18, 19]. The usable volume of this chamber has diameter of 12 mm and height of 10 mm, and the maximum achievable hydrogen/deuterium pressure amounts to 2 GPa (20 kbar). Our experiments were carried out at an average deuterium pressure of about 9 kbar (one experiment's duration 72 h, and another one 480 h) at a constant temperature of $125\,^{\circ}$C inside the chamber. All parameters (temperature, electrical resistance of controlling Pd wire, and pressure) were measured and controlled for during the whole processes. The change of resistances of Pd wire allows one to measure the relative concentration of D atoms in Pd wire, i.e., deuterium-metal ratio $n(\mathrm{D}) = \text{atom (D)/atom metal}$ [15, 18].

1.3. Depth Distribution of Implanted D^+ Ions to Various Materials by Elastic Recoil Detection Analysis (ERDA-RBS) (see, e.g., [20–22] and references therein). The depth-distribution measurements of implanted D^+ ions into metals and alloys were carried out using

RBS setup based on electrostatic generator (EG-5) of the I. M. Frank Laboratory of Neutron Physics (FLNP, JINR, Dubna) [16] and equipment at Scientific Research Institute of Nuclear Physics (SRINP, MSU, Moscow). Concentration dependences of light H/D atoms were measured by elastic recoil registration method (ERDA). The depth distributions of chemical complex compounds were measured by RBS method [8]. The He^+ ions with the energy of 2.3 MeV pass through the surface of studied sample under gliding angle of $\alpha = 15°$, and the average depth R_{He} is the projected range of He^+ ions at ERDA measurements. Registration of scattering hydrogen and deuterium recoils is carried out under registration angle 30° to an initial He^+-beam direction. The analyzed sample surfaces were of an ellipse shape with the axes about $a_1 \approx 1$ mm on $a_2 \approx 1/\sin\ 15° = 3.86$ mm. All obtained experimental spectra were then modeled with the help of computer code SIMNRA 6.05. The sliding angle of He^+ ions to surface was $\alpha = 15°$ and the angle of recoil registration along the direction of He^+ ions is $\theta = 30°$. The thickness of He^+ ion adsorption maylar foil was 12 μm. Chemical formula of polymeric material maylar is $[C_{10}H_8O_4]_n$ with mass density of 1.4 g/cm^3.

2. EXPERIMENTAL RESULTS

2.1. Depth Distributions of D Atoms Introduced into Pd and Pd Alloys and Some Other Materials by Saturation at 9 kbar Deuterium Gas Pressure. The experimental and simulated profiles of elastic recoil detection analysis (ERDA) by He^+ ions with an energy of 1.9 MeV under gliding angle of $\alpha = 15°$ in saturated $Pd_{0.9}Ru_{0.1}$ alloy (these samples were annealed at temperature of about 900 K during one hour) are presented in Fig. 2, *a*. The depth concentrations of D and H atoms calculated using computer code SIMNRA 6.05, are presented in Fig. 2, *b*. One can see that the summary concentrations of D and H atoms are $C_D \approx 3.9 \cdot 10^{19}$ m^{-2} with low depth spread (about $6.0 \cdot 10^{21}$ m^{-2}, i.e., ≈ 90 Å) and $C_H > 7.4 \cdot 10^{20}$ m^{-2} with big depth spread. The mass and atomic densities of all used Pd alloys including $Pd_{0.9}Ru_{0.1}$ alloy are presented in the Table.

As is well known, the manganin alloy with the chemical formula $Cu_{84}Mn_{14}Ni_2$, mass $\rho = 8.4$ g/cm^3 and atomic $n = 8.126 \cdot 10^{19}$ cm^{-3} densities is very often used as counter for measurements of gas pressure. That is the reason to measure its absorption-desorption

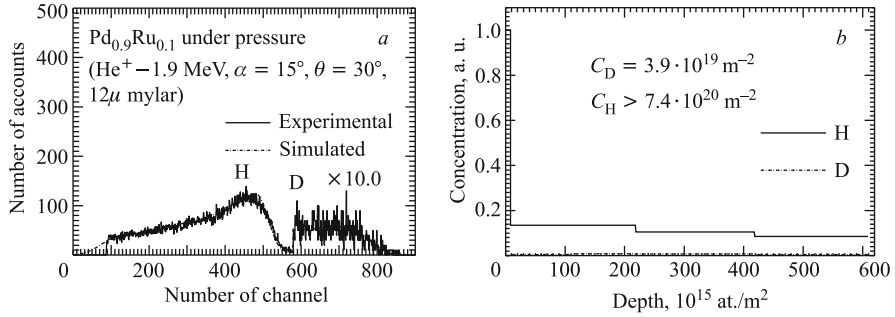


Fig. 2. The experimental and simulated spectra of H and D recoils measured by ERDA (*a*) and calculated depth concentrations of D and H atoms after saturation of $Pd_{0.9}Ru_{0.1}$ alloy under 9 kbar deuterium gas high pressure during 72 h (*b*). Measurements were carried out a long period of time after saturation

Complete summary concentrations of D (top value) and H atoms (bottom value) after implantation of D^+ ions for all studied palladium alloys: $Pd_{0.9}Ag_{0.1}$, $Pd_{0.9}Pt_{0.1}$, $Pd_{0.9}Ru_{0.1}$, and $Pd_{0.9}Rh_{0.1}$ at fluence $\Phi_1 = 1.2 \cdot 10^{22}$ m^{-2}

Summary concentrations	Pure Pd	$Pd_{0.9}Ag_{0.1}$	$Pd_{0.9}Pt_{0.1}$	$Pd_{0.9}Ru_{0.1}$	$Pd_{0.9}Rh_{0.1}$
ρ, g/cm^3	12.02	11.87	12.96	12.05	12.03
N, at. M/cm^3	$6.803 \cdot 10^{22}$	$6.798 \cdot 10^{22}$	$6.770 \cdot 10^{22}$	$6.854 \cdot 10^{22}$	$6.803 \cdot 10^{22}$
Implantation of deuterium ions, energy — 25 keV, fluence — $\Phi_1 = 1.2 \cdot 10^{22}$ m^{-2}					
R_p^{D}, Å	1237 ± 458	1267 ± 470	1227 ± 470	1255 ± 466	1264 ± 473
S, at. M/at. D	0.00112	0.0104(Pd) 0.00086(Ag)	0.0083(Pd) 0.00062(Pt)	0.0073(Pd) 0.00084(Ru)	0.00074(Pd) 0.00098(Rh)
Equation (2)	$n(D^+) \approx 1.42$ at. D^+/at. M at depth ≈ 1450 Å				
ERDA measurements after implantation (FLNP, JINR, He^+ — 2.3 MeV)					
R_p^{He}, μm	0.88 ± 0.30	0.89 ± 0.30	0.88 ± 0.32	0.87 ± 0.30	0.88 ± 0.28
C_{D}, m^{-2}	$\sim 0.45 \cdot 10^{21}$	$\sim 0.3 \cdot 10^{21}$	$\sim 0.3 \cdot 10^{21}$	$\sim 0.3 \cdot 10^{21}$	$\sim 0.3 \cdot 10^{21}$
C_{H}, m^{-2}	$> 2.4 \cdot 10^{21}$	$> 1.7 \cdot 10^{21}$	$> 1.6 \cdot 10^{21}$	$> 2.4 \cdot 10^{21}$	$> 3.2 \cdot 10^{21}$
ERDA measurements two months after implantation (MSU, He^+ — 1.9 MeV)					
C_{D}, m^{-2}	—	$\sim 0.2 \cdot 10^{21}$	$\sim 0.3 \cdot 10^{21}$	$\sim 0.3 \cdot 10^{21}$	$\sim 0.2 \cdot 10^{21}$
C_{H}, m^{-2}	—	$> 1.1 \cdot 10^{21}$	$> 1.0 \cdot 10^{21}$	$> 0.7 \cdot 10^{21}$	$> 1.1 \cdot 10^{21}$

hydrogen and its heavier isotopes properties, too. The experimental and simulated spectra of H and D recoils and calculated depth concentrations of D and H atoms after saturation of manganin under 9 kbar deuterium gas high pressure during 72 h are presented in Fig. 3, *a, b*, respectively. Measurements were carried out after long period of saturation time, too. There was observed the following: the summary concentrations of D and H atoms are $C_{\mathrm{D}} \approx 1.5 \cdot 10^{20}$ m^{-2} with low depth spread (about $4.0 \cdot 10^{21}$ at./m^2, i.e., ≈ 50 Å) and $C_{\mathrm{H}} > 1.7 \cdot 10^{21}$ m^{-2} with large depth spread.

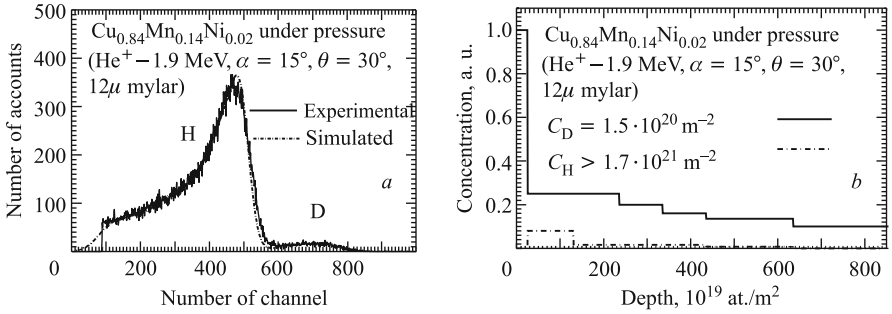


Fig. 3. The experimental and simulated spectra of H and D recoils measured by ERDA (*a*) and calculated depth concentrations of D and H atoms after saturation of manganin alloy sample under 9 kbar deuterium gas high pressure during 72 h (*b*). Measurements were carried out a long period of time after saturation

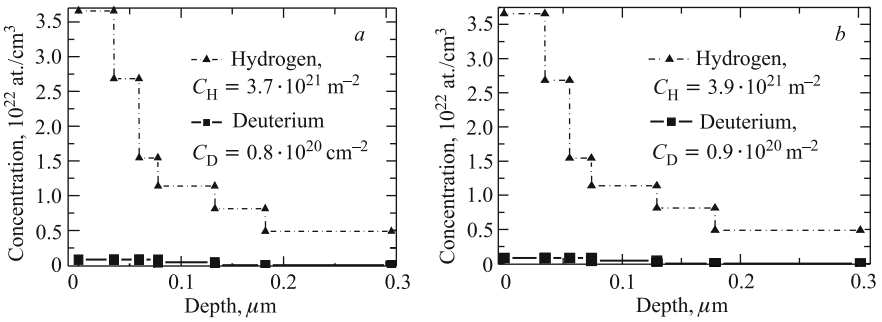


Fig. 4. ERDA depth concentrations of D and H atoms after saturation of annealed manganin sample (at 125 °C, one hour) under 9 kbar deuterium gas high pressure during 72 h. Measurements were carried out one month after saturation on the same sample just in different places ((*a*) and (*b*)) for detailed comparison of result repetition

By the way, it is seen from Figs. 2, *a* and 3, *a* that the deuterium atoms really are present in samples (see deuterium parts of spectra in these figures) and occupy the narrow surface layers in both $Pd_{0.9}Ru_{0.1}$ and manganin alloys (see deuterium parts of spectra in Figs. 2, *b* and 3, *b*).

The ERDA depth concentrations of D and H atoms after saturation of annealed manganin sample (at 125 °C, one hour) under 9 kbar deuterium gas high pressure during 72 h are presented in Fig. 4, *a, b*. Measurements were carried out one month after saturation on the same sample just in different places for detailed comparison of result repetition. As is seen, both the measurements and the obtained values are very close: $C_H^a > 3.74 \cdot 10^{21}$ m^{-2}, $C_D^a \approx 0.083 \cdot 10^{21}$ m^{-2} and $C_H^b > 3.86 \cdot 10^{21}$ m^{-2}, $C_D^b \approx 0.086 \cdot 10^{21}$ m^{-2}, i.e., there is a good repetition of results.

Besides that, it is very important to understand the influence of annealing conditions (temperature of annealing, chemical composition of annealed media, and duration of annealing) on technological hydrogen depth concentration and difference in initial and annealed samples of manganin alloy. The main reason of the deuterium gas atom usage instead of hydrogen was to separate the technological hydrogen impurities and implanted or saturated hydrogen/deuterium atoms in the studies. So ERDA depth concentrations of D and H atoms in the so-called initial (i.e., without saturation or implantation) manganin samples: annealed sample (at 125 °C, one hour) — histogram (*a*) and without annealing — histogram (*b*), are presented in Fig. 5. The summary concentrations of hydrogen atoms are $C_H^a > 3.73 \cdot 10^{21}$ m^{-2} (annealed sample) and $C_H^b > 2.32 \cdot 10^{21}$ m^{-2} (without annealing). So one can conclude from our measurements that annealing increases the absorption value of manganin alloy by a factor of about $C_H^a / C_H^b \approx 1.6$ with high accuracy of measurements. But the difference between measurements of hydrogen concentrations in the same sample after long period between measurements is very close (see comments below and Fig. 4 with summary concentrations of C_H and C_D).

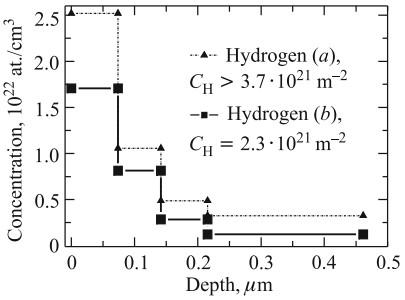


Fig. 5. ERDA depth concentrations of D and H atoms in manganin samples: annealed sample (at 125 °C, one hour) — histogram (*a*) and without annealing — histogram (*b*)

One can conclude that annealing of manganin allows one to increase the absorption value of hydrogen, and it is the reason of the usage of such counters for measuring of pressure in high pressure regime (see also R. Wisniewski [19]).

ERDA depth concentrations of D and H atoms after saturation of annealed (at 125 °C, one hour) manganin sample under 10 kbar deuterium gas high pressure during twenty days at 127 °C are shown in Fig. 6. These more recent measurements were carried out 5 days after saturation. The following results concerning summary concentrations were obtained: $C_{\mathrm{H}} > 4.22{\cdot}10^{21}$ m^{-2} with large depth spread, $C_{\mathrm{D}} \approx 0.080 \cdot 10^{21}$ m^{-2} with low depth spread.

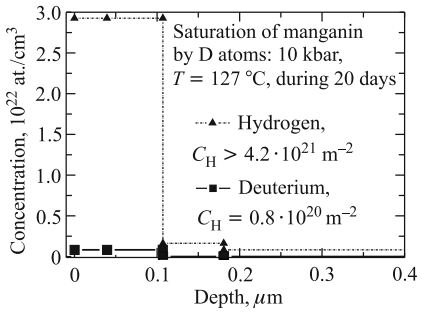


Fig. 6. ERDA depth concentrations of D and H atoms after saturation of annealed (at 125 °C, one hour) manganin sample under 10 kbar deuterium gas high pressure during twenty days at 127 °C temperature. Measurements were carried out 5 days after saturation

It is possible to conclude that increasing time of saturation (about twenty days at more suitable temperature 125 °C for manganin annealing) increases summary concentration of hydrogen in comparison with respective hydrogen summary concentration at short duration annealing time (see Fig. 4, *a, b*), but with the same deuterium concentrations! Just it is necessary to note that this conclusion needs to satisfactory check.

ERDA depth concentrations of D and H atoms for the $Pd_{0.95}Ru_{0.05}$alloy and Zr pure metal underwent deuterium gas saturation at 10 kbar pressure during twenty days at temperature of 127 °C are presented in Figs. 7 and 8, respectively. One can conclude that in both materials, $Pd_{0.95}Ru_{0.05}$ and Zr, summary concentrations of H and D atoms are similar, i.e., $C_{\mathrm{H}}^{\mathrm{Pd_{0.95}Ru_{0.05}}} < 1.3 \cdot 10^{21}$ m^{-2} with low large depth spread, $C_{\mathrm{D}}^{\mathrm{Pd_{0.95}Ru_{0.05}}} > 2.1 \cdot 10^{21}$ m^{-2} with large depth spread and $C_{\mathrm{H}}^{\mathrm{Zr}} < 1.3{\cdot}10^{21}$ m^{-2} with low large depth spread, $C_{\mathrm{D}}^{\mathrm{Pd_{0.95}Ru_{0.05}}} > 2.4 \cdot 10^{21}$ m^{-2} with large depth spread. So it would be better to repeat these measurements after about a few months of saturation time, to understand whether the exchange-replace of

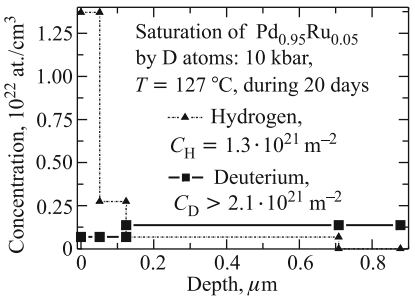


Fig. 7. ERDA depth concentrations of D and H atoms after saturation of annealed (at 125°C, one hour) $Pd_{0.95}Ru_{0.05}$ sample under 10 kbar deuterium gas high pressure during twenty days at temperature 127 °C. Measurements were carried out 5 days after saturation

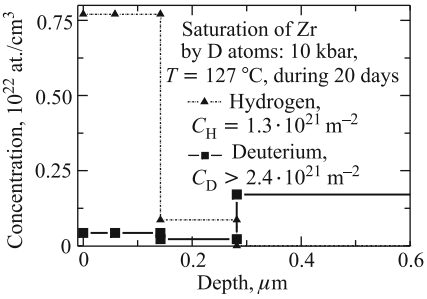


Fig. 8. ERDA depth concentrations of D and H atoms after saturation of annealed (at 125°C, one hour) pure zirconium sample under 10 kbar deuterium gas high pressure during twenty days at temperature 127 °C. Measurements were carried out 5 days after saturation

depth and summary concentrations between hydrogen and deuterium will take place here as it was in previous results concerning mainly the behavior of $Pd_{0.9}Ru_{0.1}$alloy (see Fig. 2 and Figures below).

2.2. Depth Distribution of Implanted D^+ Ions into Pd and Its Diluted Alloys. The ERDA summary and depth concentrations of D and H atoms after implantation of D^+ ions up to a fluence of $\Phi = 1.2 \cdot 10^{22}$ m^{-2} (*a*) and saturation under 9 kbar deuterium gas during three days of $Pd_{0.9}Ru_{0_1}$ and $Pd_{0.9}Ag_{0.1}$ samples (*b*) are presented in Figs. 9 and 10. All measurements were carried out three month after implantation and saturation. The summary concentrations of D and H atoms were $C_H > 7.1 \cdot 10^{20}$ m^{-2} with large depth spread and $C_D \approx 2.7 \cdot 10^{20}$ m^{-2} with low depth spread (for $Pd_{0.9}Ru_{0.1}$ alloy) and $C_H > 7.4 \cdot 10^{20}$ m^{-2} with large depth spread and $C_D \approx 3.9 \cdot 10^{19}$ m^{-2} with low depth spread (for $Pd_{0.9}Ag_{0.1}$alloy). Summary concentrations of hydrogen in both cases (implantation and saturation into $Pd_{0.9}Ru_{0.1}$ alloy) are very close and summary concentrations of deuterium in the case of implantation are about 10 times more in comparison with saturation treatment. Similar behavior in the comparative analysis for $Pd_{0.9}Ag_{0.1}$ alloy just differs a little bit less. From our point of view, the differences between implanted and saturated summary concentrations of deuterium atoms into Pd diluted

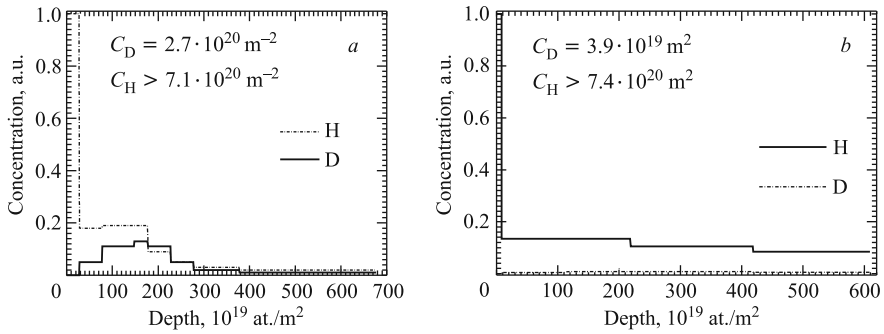


Fig. 9. ERDA depth concentrations of D and H atoms after implantation of D^+ ions up to a fluence of $\Phi = 1.2 \cdot 10^{22}$ m^{-2} (*a*) and saturation under 9 kbar deuterium gas during three days of $Pd_{0.9}Ru_{0.1}$ sample (*b*). Measurements were carried out 30 days after saturation and implantation

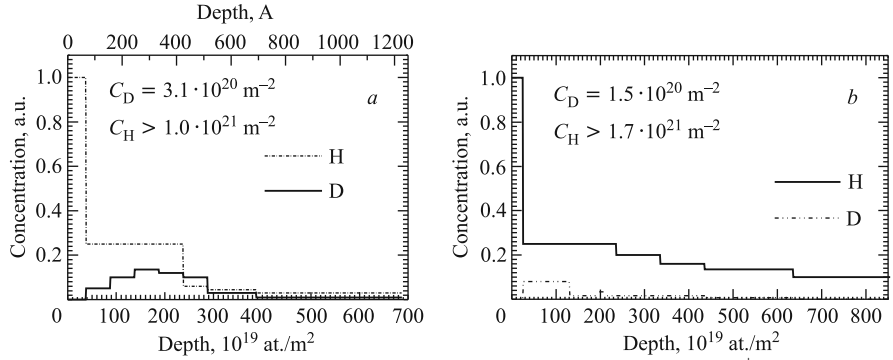


Fig. 10. ERDA depth concentrations of D and H atoms after implantation of D^+ ions up to a fluence of $\Phi = 1.2 \cdot 10^{22}$ m^{-2} (*a*) and saturation under 9 kbar deuterium gas during three days of $Pd_{0.9}Ag_{0.1}$ sample (*b*). Measurements were carried out three months after implantation and saturation

alloys can be explained by capturing of implanted deuterium atoms by radiation traps produced by elastic scattering implanted ions with the energy of 25 keV and displacements of lattice atoms with creation of damage clusters as gas bubbles and vacancies and interstitial loops [8–13, 23, 24].

We show here the following approach: we measure, using some various methods (ERDA of course, too), the summary and depth concentrations of D and H atoms in Pd and its diluted alloys implanted up to high fluence of D^+ ions and saturated by D atoms at high pressure after long time of such treatments which should allow one to estimate the concentration of radiation stimulating-creating deuterium traps as a difference between measured values in both cases.

Other ERDA measured depth-dependent concentrations of D and H atoms for a pair of measurements: about 10 days (*a*) and three months (*b*) later after implantation, are presented in Figs. 11–15.

One can see from these Figures that after long period of time between the first and second ERDA measurements, the concentrations of D atoms practically do not change. Also it is necessary to note that practically in all samples (excluding $Pd_{0.9}Ru_{0.1}$ alloy) hydrogen atom concentrations are very high and on very large depth from the surface of samples, i.e., much

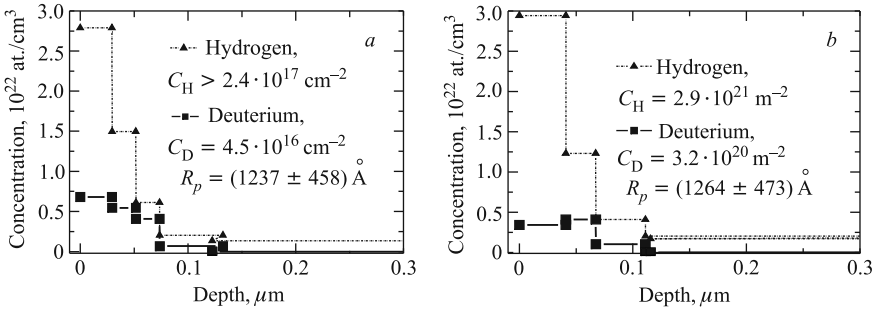


Fig. 11. The depth concentrations of D and H atoms after implantation of D^+ ions with the energy of 25 keV at a fluence of $\Phi_1 = 1.2 \cdot 10^{22}$ m^{-2} in pure Pd (*a*) and $Pd_{0.9}Ag_{0.1}$ (*b*) samples

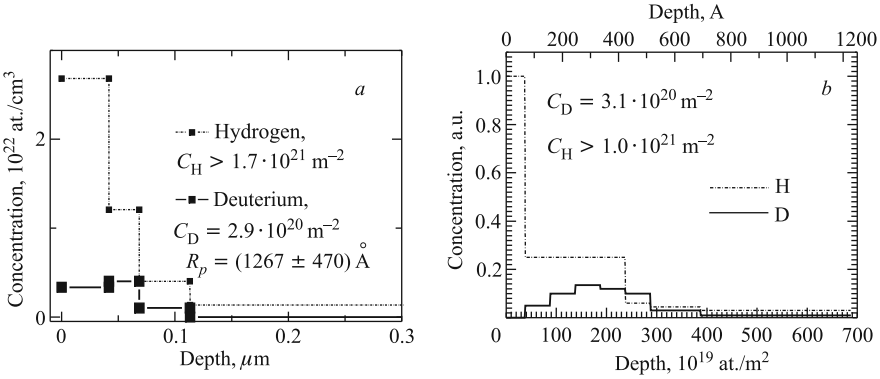


Fig. 12. The depth concentrations of D and H atoms after D^+-ion implantation with the energy of 25 keV at a fluence of $\Phi_1 = 1.2 \cdot 10^{22}$ m^{-2} in $Pd_{0.9}Ag_{0.1}$ samples 10 days after (*a*) and three months later (*b*)

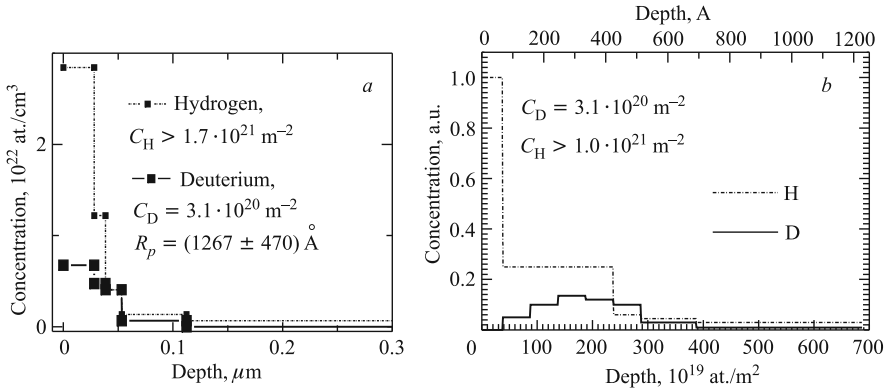


Fig. 13. The depth concentrations of D and H atoms after D^+-ion implantation with the energy of 25 keV at a fluence of $\Phi_1 = 1.2 \cdot 10^{22}$ m^{-2} in $Pd_{0.9}Pt_{0.1}$ samples 10 days after (*a*) and three months later (*b*)

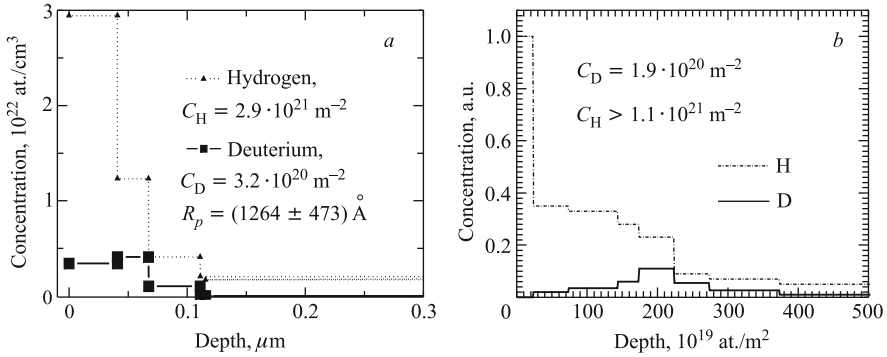


Fig. 14. The depth concentrations of D and H atoms after D^+-ion implantation with the energy of 25 keV at a fluence of $\Phi_1 = 1.2 \cdot 10^{22}$ m^{-2} in $Pd_{0.9}Rh_{0.1}$ samples 10 days after (*a*) and three month later (*b*)

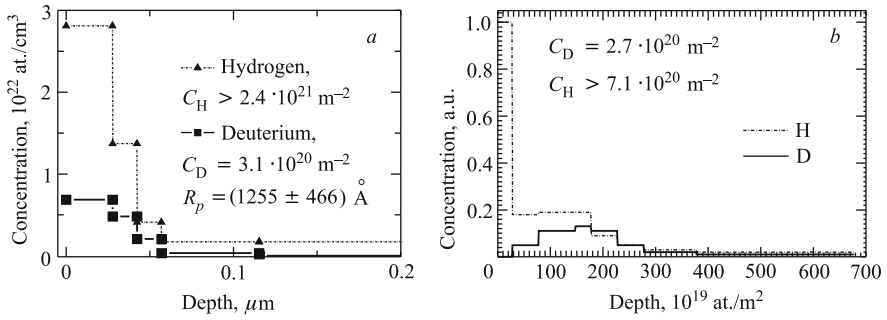


Fig. 15. The depth concentrations of D and H atoms after D^+-ion implantation with the energy of 25 keV at a fluence of $\Phi_1 = 1.2 \cdot 10^{22}$ m^{-2} in $Pd_{0.9}Ru_{0.1}$ samples 10 days after (*a*) and three month later (*b*)

more than the measured ERDA layer by He^+ ions (see the projected ranges — R_p^{He} in the Table). Some differences between measured values can be connected also with different energies of ERDA methodics in FLNP-JINR and in SRINP-MSU — 2.3 and 1.9 MeV, respectively. It is necessary to note the last measured fact — high long-depth hydrogen concentrations should be checked again before implantation in pure Pd and Pd-alloy samples. The keeping of summary concentrations of D atoms in measured Pd and Pd alloys can be explained by absorption of D atoms in gas bubbles and probably in grain boundaries [9–13].

The complete ERDA measurement results of summary D- and H-atom concentrations in Pd and some palladium-based alloys as: $Pd_{0.9}Ag_{0.1}$, $Pd_{0.9}Pt_{0.1}$, $Pd_{0.9}Ru_{0.1}$, and $Pd_{0.9}Rh_{0.1}$ are presented in the Table. It is necessary to note that depth distributions of the so-called technological hydrogen atoms are very deep and have high summary values for all Pd alloys. The conclusion is: both components of D and H atoms do not participate in desorption processes and exist in alloy lattices as gas atoms absorbed and trapped, i.e., mainly as substitutive impurities or in small gas bubbles [9–13]. The achieved concentrations of hydrogen atoms are high at $(1.5{-}3.2) \cdot 10^{21}$ m^{-2} which is very promising for possible future applications of that type of energy storage. The depth distributions of H atoms have a wide spread on large depth from surfaces for all studied Pd alloys. The absence of differences between long period measurements allows one to conclude that both components of D ions and H atoms do not participate in desorption processes and exist in alloy lattices as gas atoms absorbed and captured traps, i.e., mainly as substitutive impurities or in small gas bubbles [9–13].

CONCLUSION

There is one good approach to measure, using some various methods (ERDA of course, too), the summary and depth concentrations of D and H atoms in Pd and its diluted alloys implanted up to a high fluence of D^+ ions and saturated by D atoms at high pressure after long time of such treatment which should allow one to estimate the deuterium concentration by using the radiation stimulating created traps.

One can conclude that annealing of manganin allows one to increase the absorption value of hydrogen, and it is the reason of the usage of such counters for pressure measuring in high pressure regime (see also R. Wisniewski [19]).

In spite of very high fluence of implantation into all studied materials, no effects connected to blistering and flaking phenomena were observed.

There were observed very small desorption and spread of D^+-implanted layers into Pd and its diluted alloys, also there were detected long depth and high concentrations of hydrogen atoms in these samples.

It is possible to conclude that increasing time of saturation (about twenty days at more suitable temperature of $125\,^\circ$C for manganin annealing) increases summary concentration of hydrogen much more in comparison to short duration annealing time (see Fig. 4, *a, b*) and respective hydrogen summary concentrations and the same deuterium concentrations. Just it is necessary to note that this conclusion needs to satisfactory check.

Also one can note that ERDA measurements of deuterium concentrations after various treatments of different materials allow one to get with consequent parameters of samples very interesting and important results and very quickly.

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