

Characteristics of hydride-like segregates of hydrogen at dislocations in palladium

Yu S Nechaev

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Abstract. On the basis of multifactor analysis of the most representative experimental data on the solubility, electrical resistance, and diffusivity of hydrogen in palladium specimens with high and low dislocation densities, it has been shown that the structure, composition, diameter (up to several nm), contribution to electrical resistance, thermodynamic and diffusion characteristics of hydride-like segregates at dislocations in palladium can vary in wide limits depending on the concentration and thermodynamic activity of hydrogen dissolved in the normal lattice of the metal. The formation of hydride-like segregation phases at dislocations occurs at high degrees of undersaturation of the solid solutions with respect to the hydride precipitation in the normal lattice of palladium. This means that a specific phase diagram can be considered for a 'hydrogen — near-dislocation segregation Pd nanoregions' system, in comparison with the conventional hydrogen–palladium phase diagram. The results obtained can be used for the description of the apparent concentration and distribution of hydrogen between the normal crystal lattice and defect regions

in palladium specimens produced using different processing and treatment methods. In particular, the results can be used for the interpretation of hydrogen influence on the physical and mechanical properties of the materials, and also for revealing the micromechanisms and ways of the optimization of regimes of thermal-hydrogen treatment and governing hydrogen-induced transformation hardening of palladium and palladium-based alloys.

1. Introduction

Hydrogen, which dissolves and diffuses in metals and alloys, interacts with the lattice defects that can serve as hydrogen traps (dislocations, vacancies, grain boundaries, voids, impurities, second-phase precipitates, and others). These traps, mainly dislocations, influence the apparent characteristics of hydrogen solubility and diffusivity [1, 2]; as a result, even small additions of hydrogen can significantly affect the physical, mechanical, and corrosion properties of metals and alloys [3, 4]. This influence essentially depends on the methods of preparation and treatment of materials, resulting in different contents of lattice defects, and it especially manifests itself under the so-called thermal-hydrogen treatment and hydrogen induced transformation hardening of a number of metallic materials [3, 4], including palladium and palladium-based alloys. These micromechanisms of hydrogen influence have been studied insufficiently [4], which is to a considerable degree caused by the absence of a sufficiently complete database on the characteristics and nature of hydrogen segregation at dislocations.

Yu S Nechaev I P Bardin Central Research Institute of Iron and Steel Industry, Institute of Metal Physics
2-ya Baumanskaya ul. 9/23, 105007 Moscow, Russian Federation
Tel./Fax (7-095) 777-93 50
E-mail: netchaev@online.ru

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The experimental methods of studying dislocation-type hydrogen traps and their influence on the apparent characteristics of hydrogen solubility and diffusivity in metallic materials are described in [5, 6]. For the treatment and interpretation of the experimental data on hydrogen diffusion obtained by various methods [5, 6], the Oriani model [2] or the McNabb–Foster model [7, 8] (which is equivalent to the Oriani one, but only for the case of a small filling [7] of the traps) are usually applied.

The McNabb–Foster model [7, 8] is also widely applied for the case of high filling of the traps [5]. However, this appears to be incorrect, since in this model [7, 8] the local-equilibrium approximation and a Boltzmann-type distribution law or the Henry-type absorption isotherm are used, which correspond to the case of a small filling of the traps. As is shown in Sections 4 and 5 of the present paper, the Oriani model [2] is used in some works [5, 6] beyond the applicability limits, which may lead to an inadequate treatment and interpretation of experimental data.

For determination of the characteristics of hydrogen traps (of which the most significant in deformed or martensite structures are hydrogen segregates at dislocations [9, 10]) from the experimental data [5, 6] on the hydrogen solubility, diffusivity, and electrical resistance, it is necessary to use a complex methodological approach — multifactor physicochemical analysis [9–15]. This approach is presented in the given paper for the example of palladium, for which the largest body of corresponding experimental data [6, 16–21] exists in comparison with other metals and alloys. It should be emphasized that up to date the data of [6, 16–21] remain the most representative and detailed, and also the most cited. At the same time, the treatment and interpretation of the data in the works [6, 16–21] are not sufficiently complete, and in some cases, as the results of the analysis presented below show, they are not sufficiently grounded, and a definite correction seems expedient. In the present work, special attention is given to the consideration of the influence of linear defects (dislocations), produced by different ways of preparing and treating the material (Pd), on the total concentration of hydrogen, its distribution in the material, and its local state in the lattice-defect regions. Note that these aspects are usually not considered in the framework of the conventional phase diagram of the ‘hydrogen–palladium’ system.

2. Critical analysis of the treatment and interpretation of Flanagan’s data [16] on the hydrogen solubility in deformed and annealed palladium

In the widely known work by Flanagan [16], experimental data are presented on the solubility enhancements for hydrogen in heavily cold-worked (by milling or filing) and in deformed by cold rolling (to a strain degree of $\varepsilon = 78\%$) specimens of α palladium at 273–363 K in comparison with annealed specimens. When interpreting their results, the authors of [16, 17] supposed that the elastic stress field of the dislocation array in the metal lattice between dislocations is the principal cause of the observed solubility enhancements. They neglected the possibility of hydrogen absorption at the dislocation cores, and also the possibility of formation of segregation phases at dislocations.

In this section, a critical analysis of the results of [16, 17] is presented. It has been shown that the solubility enhancements

observed in [16] are mainly caused by the formation of hydride-like segregation atmospheres at dislocations (several nanometers in size), without an essential change in the hydrogen solubility in the metal lattice between dislocations.

When describing the solubility enhancements observed in [16] using the model developed in [17], the authors of these works varied two parameters: the dislocation core radius (r_c) and the dislocation density (ρ_\perp). For the heavily cold-worked Pd specimens, a satisfactory description was obtained, for instance, for $r_c = 2b$ (where $b = 0.275$ nm is the magnitude of the smallest Burgers vector in Pd) and $\rho_\perp = 9 \times 10^{15} \text{ m}^{-2}$ [17].

In the framework of the dislocation theory [22], the hydrostatic pressure P_\perp in the tensile-stress regions can reach 5.4×10^9 Pa at a distance $r_c = 2b$ from the dislocation lines, 3.6×10^9 Pa at a distance $r_c = 3b$, and 2.2×10^9 Pa at a distance of $5b$.

The local hydrogen concentration C_\perp (the H-to-Pd atom ratio) in the near-dislocation segregation regions (NDSRs) under a pressure P_\perp can be evaluated in the Bragg–Williams approximation, using the Fowler–Guggenheim isotherm equation [11, 16, 22, 23]

$$\frac{\theta_\perp(1-\theta)}{\theta(1-\theta_\perp)} \approx \exp \left\{ \frac{P_\perp \Delta V_H - 2(W_{\perp H-H} \theta_\perp - W_{H-H} \theta)}{RT} \right\}, \quad (1)$$

where $\theta_\perp = C_\perp/C_{\perp \max}$; $C_{\perp \max}$ is the maximum possible hydrogen concentration in the NDSR; $\theta = C/C_{\max}$; C is the hydrogen concentration (the H-to-Pd atom ratio) in the metal lattice without dislocations; $C_{\max} = 1$ for Pd in which there is one octahedral interstice for hydrogen per one Pd atom; the sign of P_\perp is positive in the tensile-stress near-dislocation regions (in the NDSR) [17]; the partial molar volume of hydrogen in the metal is $\Delta V_H = (1.65 \pm 0.05) \times 10^{-6} \text{ m}^3 (\text{mol(H)})^{-1}$ [17]; the parameter of the pairwise H–H attractive interaction $W_{H-H} = -23.4 \pm 0.5 \text{ kJ mol}^{-1}$ for $C = (1-30) \times 10^{-3}$ [16, 17]; $W_{\perp H-H}$ is the parameter of the H–H interaction for higher concentrations (C_\perp); R is the gas constant; and T is the temperature (in Kelvins).

By using Eqn (1) and taking $C = \theta = 1 \times 10^{-2}$, $T = 320$ K, and $W_{\perp H-H} \approx W_{H-H}$, one can show that the θ_\perp values for $r_c = 2b$ and $r_c = 3b$ are close to unity; i.e., the composition of the segregates is close to PdH if $C_{\perp \max} = 1$; for $r_c = 5b$, the θ_\perp value is about 0.1. These estimates show the possibility of the formation of hydride-like segregation atmospheres of nanometer diameter in the tensile-stress regions near dislocations.

In the case of large enough radii of the hydride-like segregation atmospheres, the effect of the dislocation stress field on the hydrogen solubility in the metal lattice can be negligible. The number of excess hydrogen atoms (due to the dislocation-stress-field influence) per dislocation length b can be evaluated using the expression [22]

$$n_H \approx \frac{\pi \beta^2 C}{2b^2 k^2 T^2} \ln \left(\frac{L}{r_c} \right), \quad (2)$$

where $\beta = \mu b(1+\nu)\Delta V_H/3\pi N_A(1-\nu)$; $L \approx (1/2)\rho_\perp^{-1/2}$; μ is the shear modulus of the metal; ν is Poisson’s ratio of the metal; N_A is Avogadro’s number; and k is the Boltzmann constant. Expression (2) is valid if $r_c > \beta/kT = 1.8 \times 10^{-9}$ m for $T = 320$ K. Hence, for $C = 1 \times 10^{-2}$, $r_c = 2 \times 10^{-9}$ m, and $L = 5 \times 10^{-9}$ m, n_H is about 1; the excess solubility $\Delta C \approx n_H \rho_\perp b^2 = 7.6 \times 10^{-4}$ for $\rho_\perp = 1 \times 10^{16} \text{ m}^{-2}$.

The possibility of the formation of hydride-like segregation atmospheres at dislocations (HLSAD) is confirmed by the observation [16] of the absence of an appreciable hydrogen supersaturation during the transformation of the metal (α -Pd) to the nonstoichiometric hydride β phase (of Pd₂H type) in cold-worked specimens, in contrast to the situation for the well-annealed specimens (see Fig. 8 from [16]). Obviously, this may be caused by the high content of HLSADs in the cold-worked specimens, which are ready nuclei of the hydride phase (see also Sections 3 and 5 of this paper).

As has been shown in [24], the results of [16] cannot be explained by only the elastic stress field of the dislocation array. An 'extended-core model' has been proposed [24], characterized by an effective binding enthalpy (of about 3.3 kJ mol⁻¹ for Pd) within an extended core of radius $r_c = 10b$. However, as is noted in [19], the extended-core model [24] is not able to explain the results [18] for specimens with low hydrogen content. It is also noted [19] that in the framework of the model [24], the term 'extended core' can be replaced by the term 'hydride-like segregation phase'.

3. Influence of the segregation atmospheres at dislocations on the apparent characteristics of hydrogen solubility in Pd: a re-treatment of the data of [16]

The equilibrium state of the process of dissolution ($1/2 \text{ H}_2 \rightarrow [\text{H}]_V$) of gaseous hydrogen in the metal volume (undisturbed lattice) between dislocations, where the influence of their elastic stress field can be neglected, is described [16, 23] as follows:

$$\frac{\theta}{1-\theta} = \left(\frac{P_{\text{H}_2}}{P_{\text{H}_2}^0} \right)^{1/2} \exp \left\{ - \frac{(\Delta H_{\text{H}}^0 - T\Delta S_{\text{H}}^0) + 2W_{\text{H-H}}\theta}{RT} \right\}, \quad (3)$$

where P_{H_2} is the equilibrium hydrogen pressure over the metal (the solid solution); $P_{\text{H}_2}^0$ is the pressure of hydrogen in its standard state; $\Delta H_{\text{H}}^0 = -10 \pm 0.2 \text{ kJ (mol(H))}^{-1}$ and $\Delta S_{\text{H}}^0 = -54.7 \pm 1 \text{ J (K mol(H))}^{-1}$ are the standard changes of enthalpy and entropy of the process; the standard state implies the ideal dilution of the solid solution ($\theta^0 \rightarrow 0$) [16].

The mass action law for this process can be presented as

$$\frac{a_{\text{H}}}{(P_{\text{H}_2}/P_{\text{H}_2}^0)^{1/2}} = \exp \left\{ - \frac{(\Delta H_{\text{H}}^0 - T\Delta S_{\text{H}}^0)}{RT} \right\},$$

where $a_{\text{H}} = \gamma C$ is the thermodynamic activity of hydrogen in the metal (Pd) lattice without stresses and dislocations; in the standard state of the solid solution, we have $a_{\text{H}}^0 = \theta^0 \rightarrow 0$, $P_{\text{H}_2} \rightarrow 0$. The activity coefficient of hydrogen in the Pd lattice (the solid solution) is described as

$$\gamma \approx \frac{1}{1-\theta} \exp \left\{ \frac{2W_{\text{H-H}}\theta}{RT} \right\};$$

for $C = 1 \times 10^{-2}$ and $T = 323 \text{ K}$, we obtain $\gamma \approx 0.85$.

The thermodynamic factor [6] of the chemical diffusion coefficient for hydrogen in the metal (Pd) lattice is described by the expression

$$f_{\text{H}} = \frac{\partial \ln a_{\text{H}}}{\partial \ln C} = \frac{1 + \theta(1-\theta)2W_{\text{H-H}}/RT}{1-\theta};$$

for $C = 1 \times 10^{-2}$ and $T = 323 \text{ K}$, we have $f_{\text{H}} \approx 0.83$.

If the standard state of the solid solution refers to $\theta^0 = 1/2$, i.e., to the Pd₂H composition, then Eqn (3) can be transformed [23] into

$$\frac{\theta}{1-\theta} = \left(\frac{P_{\text{H}_2}}{P_{\text{H}_2}^0} \right)^{1/2} \times \exp \left\{ - \frac{(\Delta H_{\text{H}}^0 - T\Delta S_{\text{H}}^0 + W_{\text{H-H}}) + W_{\text{H-H}}(2\theta - 1)}{RT} \right\}. \quad (3')$$

Here, the coefficient of the thermodynamic activity of hydrogen in the metal lattice (in the absence of the concentration dependence of $W_{\text{H-H}}$ in the interval from $\theta \approx 0$ to 0.5) is described by the expression

$$\gamma \approx \frac{1}{1-\theta} \exp \left\{ \frac{W_{\text{H-H}}(2\theta - 1)}{RT} \right\};$$

for $C = 1 \times 10^{-2}$ and $T = 323 \text{ K}$, we obtain $\gamma \approx 5.2 \times 10^3$; the value of the equilibrium constant of the reaction also changes in the corresponding manner. The thermodynamic factor f_{H} is described by the same expression as for the previous case (for $\theta^0 \rightarrow 0$). A value of $f_{\text{H}} \approx 0.83$ is obtained (for the same C and T), that is, this quantity does not depend on the choice of the standard state for the solution.

The equilibrium state of the reaction $1/2 \text{ H}_2 \rightarrow [\text{H}]_{\perp}$ of gaseous hydrogen dissolving in the near-dislocation segregation regions (NDSRs) under hydrostatic pressure P_{\perp} in palladium can be approximated [11, 22, 23] as follows:

$$\frac{\theta_{\perp}}{1-\theta_{\perp}} \approx \left(\frac{P_{\text{H}_2}}{P_{\text{H}_2}^0} \right)^{1/2} \times \exp \left\{ - \frac{(\Delta H_{\text{H}}^0 - T\Delta S_{\text{H}}^0) - P_{\perp}\Delta V_{\text{H}} + 2W_{\perp\text{H-H}}\theta_{\perp}}{RT} \right\}; \quad (4)$$

equation (1) for the equilibrium state of the reaction $[\text{H}]_{\text{V}} \rightarrow [\text{H}]_{\perp}$ can be obtained by dividing Eqn (4) by Eqn (3).

The previous consideration (Section 2) using Eqn (1) has shown the possibility of hydrogen clustering in Pd (to a hydride-like structure) in the regions of tension of nanometer diameter at dislocations, i.e., the possibility of the formation of HLSADs in the NDSRs. The cross section of the NDSR or HLSAD can be approximated by the contour of constant pressure [6, 11, 22]

$$P_{\perp} \approx \frac{\mu b(1+\nu)}{6\pi(1-\nu)r_s}, \quad (5)$$

where $r_s \approx r_c/2 \sin \varphi$ is the NDSR (HLSAD) radius; φ is the angle between the dislocation and its glide plane; and the P_{\perp} estimates for $2r_s$, $2b$, $3b$, and $5b$ are presented in Section 2.

Averaging the radial gradient distribution of the composition, structure, and properties of the NDSR (HLSAD) at their definite effective radius r_s gives ground to consider these regions as one-dimensional nanophases, i.e., as tubes with a diameter of a nanometer order.

The mass action law for the hydrogen transition from the Pd lattice to the structure of the NDSR (HLSAD) can be also approximated by the expression [11, 23, 25]

$$\frac{a_{\perp\text{H}}}{a_{\text{H}}} \approx \exp \left\{ \frac{(P_{\perp} - (\sigma/r_s))\Delta V_{\text{H}} + (\Delta H_{\text{H}}^0 - \Delta H_{\text{H}}^0)}{RT} \right\},$$

where $a_{\perp H} = \gamma_{\perp} C_{\perp}$ and $a_H = \gamma C$ are the thermodynamic activities of hydrogen in the NDSR (HLSAD) and the metal lattice, respectively; ΔV_h and ΔH_h^0 are the volume and enthalpy changes for the process of formation of the segregate structure of the Pd_xH type; σ is the surface tension for the Pd / Pd_xH interface; and $P_{\perp} > \sigma/r_S$ [11, 25]. The coefficient of the thermodynamic activity of hydrogen in the NDSR (HLSAD) of variable composition x can be approximated by the expression

$$\gamma_{\perp} \approx \left[\frac{\theta_{\perp}}{C_{\perp}(1 - \theta_{\perp})} \right] \exp \left\{ \frac{2W_{\perp H-H}\theta_{\perp}}{RT} \right\}.$$

The thermodynamic factor of the chemical diffusion coefficient of hydrogen in the NDSR (HLSAD) can be presented as

$$f_{\perp H} = \frac{1 + \theta_{\perp}(1 - \theta_{\perp})2W_{\perp H-H}/RT}{1 - \theta_{\perp}}.$$

There are some grounds [26] to suppose that the absolute value of $W_{\perp H-H}$ may be essentially lower than W_{H-H} , up to $W_{\perp H-H} \approx 0$; then, the values of $f_{\perp H}$ and γ_{\perp} may be on the order of unity.

In the framework of such an approximation, the apparent concentration of hydrogen (C_{Σ}) in palladium with a dislocation density ρ_{\perp} , including the post-clustering case of the HLSAD formation, is described by the expressions [11, 25]

$$C_{\Sigma} \approx C(1 - \eta_{\perp} + \eta_{\perp}K_{\perp}), \quad (6)$$

$$\eta_{\perp} \approx d_{\perp}^2 \rho_{\perp}, \quad (7)$$

$$K_{\perp} \approx \frac{C_{\perp}}{C} \approx \exp \left(\frac{\Delta H_b}{RT} \right) \exp \left(-\frac{\Delta S_b}{R} \right), \quad (8)$$

where $d_{\perp} = 2r_s$ is the average diameter of the NDSR or HLSAD; η_{\perp} is the atomic (volume) fraction of the NDSRs (HLSADs); K_{\perp} is the equilibrium constant; ΔH_b , ΔS_b are the apparent enthalpy and entropy of hydrogen binding with the NDSR (HLSAD); and it is supposed that $C_{\perp \max} = 1$, $C_{\max} = 1$, $a_H \approx \theta \approx C$, $\gamma \approx 1$, $a_{\perp H} \approx \theta_{\perp} \approx C_{\perp}$, and $\gamma_{\perp} \approx 1$.

The values of ΔH_b and $\eta_{\perp} \exp(-\Delta S_b/R)$ can be obtained from the linear dependence of $\ln[(C_{\Sigma} - C)/C]$ on $1/T$, where C_{Σ} corresponds to the heavily cold-worked or cold-rolled (78%) samples [16], and C , to the annealed samples [16]. Such a re-treatment of the data of [16] for the cold-rolled (to 78%) samples (saturated with hydrogen at $T = 310, 323.2$, and 363 K) yields $\Delta H_b = 13.8 \pm 3.5$ kJ (mol(H))⁻¹ and $\eta_{\perp} \exp(-\Delta S_b/R) = (1.5 \pm 1.1) \times 10^{-3}$. For the heavily cold-worked samples [16] (for $T = 273.2, 298.2, 310.7$, and 323.2 K), these quantities are $\Delta H_b = 5.0 \pm 0.5$ kJ (mol(H))⁻¹ and $\eta_{\perp} \exp(-\Delta S_b/R) = 0.081 \pm 0.015$.

The number of hydrogen atoms in the NDSR or HLSAD per dislocation length b can be described [11] as

$$n_{H\perp} \approx \frac{C_{\Sigma} - C}{\rho_{\perp} b^2}. \quad (9)$$

For the cold-rolled (to 78%) samples, assuming $\rho_{\perp} \approx 1 \times 10^{15}$ m⁻² [27] and $C_{\Sigma} - C \approx 5 \times 10^{-3}$ [16], we obtain $n_{H\perp} \approx 66$ (for the largest concentrations $C = 3.5 \times 10^{-2}$ at 363 K, 2.2×10^{-2} at 323 K, and 1.5×10^{-2} at 310 K). This value of $n_{H\perp}$ is close to the value obtained in [28] from the analysis of the same data [16].

For the heavily cold-worked samples, assuming $\rho_{\perp} \approx 9 \times 10^{15}$ m⁻² [17] and $C_{\Sigma} - C \approx 5 \times 10^{-3}$ [16], we

obtain $n_{H\perp} \approx 7$ (for the largest concentrations $C = 6.8 \times 10^{-3}$ at 273 K and 9.6×10^{-3} at 323 K).

The value of ΔH_b obtained for the specimens cold-rolled to 78% [16] is close to the enthalpy change (13 kJ (mol(H))⁻¹) for the hydrogen transition from the β phase (that is, from Pd_2H) to α -Pd evaluated in [19] using the standard thermodynamic data. Supposing the HLSAD composition in the 78%-deformed samples [16] to be about that of Pd_2H , and using the obtained value of $n_{H\perp}$ for them, their diameter d_{\perp} can be evaluated as

$$d_{\perp} \approx b(2n_{H\perp})^{1/2}. \quad (10)$$

Hence, we obtain $d_{\perp} \approx 3.2$ nm, which is in accordance with the data [6] on the neutron small-angle scattering for the cold-rolled Pd specimens ($\varepsilon = 99\%$), containing 1 at.% deuterium (C_{Σ}).

Using the above-obtained value of d_{\perp} for the 78%-deformed specimens [16] gives reasonable values of the characteristics: $\eta_{\perp} \approx 0.01$ (Eqn (7)); $\Delta S_b/R \approx 1.9$; $C_{\perp} \approx 0.48$ for $C = 1.5 \times 10^{-2}$ at 310 K (Eqn (8)); $C_{\perp} \approx 0.56$ for $C = 2.2 \times 10^{-2}$ at 323 K; $C_{\perp} \approx 0.51$ for $C = 3.5 \times 10^{-2}$ at 363 K. The obtained values of C_{\perp} obviously correspond to the HLSAD composition close to Pd_2H .

Taking for the cold-worked specimens [16] the same value of $d_{\perp} \approx 3.2$ nm results in the characteristic values $\eta_{\perp} \approx 0.09$, $\Delta S_b/R \approx 0.13$, $C_{\perp} \approx 0.05$ for $C = 6.8 \times 10^{-3}$ at 273 K and for $C = 9.6 \times 10^{-3}$ at 323 K. The lower values of ΔH_b and C_{\perp} for the heavily cold-worked specimens [16] in comparison with those cold-rolled to 78% is probably caused by the mutual interaction of dislocations (the compensation effect) in the case of the extremely large densities [22, 27].

By taking into account (i) the results of works (see review [29]) on the formation of a metastable phase $PdH_{1.1-1.3}$ at the lattice defect regions of Pd-based alloys that underwent hydrogen-induced transformation hardening, and also (ii) the calorimetric and dilatometric data [27] on the dislocation density in the cold-rolled metals at different degrees of deformation ($\rho_{\perp} = (1.4 \pm 0.4) \times 10^{15}$ m⁻² for $\varepsilon = 30\%$; $(2.0 \pm 0.5) \times 10^{15}$ m⁻² for $\varepsilon = 50\%$; $(2.6 \pm 0.9) \times 10^{15}$ m⁻² for $\varepsilon = 70\%$), slightly different values of the characteristics can be obtained using an analogous treatment of the data of [16]. Thus, assuming $\rho_{\perp} \approx 3 \times 10^{15}$ m⁻² [27] and $C_{\Sigma} - C \approx 5 \times 10^{-3}$ [16] for the specimens cold-rolled to 78%, we obtain $n_{H\perp} \approx 22$ (for $C = 3.5 \times 10^{-2}$ at 363 K, $C = 2.2 \times 10^{-2}$ at 323 K, and $C = 1.5 \times 10^{-2}$ at 310 K).

Supposing that the HLSAD composition in specimens cold-rolled to 78% is about that of PdH [29] gives [instead of Eqn (10)] the following: $d_{\perp} \approx b(n_{H\perp})^{1/2}$; hence, we obtain $d_{\perp} \approx 1.3 \times 10^{-9}$ m. This gives for the 78%-deformed specimens [16] the characteristic values $\eta_{\perp} \approx 5.1 \times 10^{-3}$, $\Delta S_b/R \approx 1.2$, $C_{\perp} \approx 0.95$ for $C = 1.5 \times 10^{-2}$ at 310 K, $C_{\perp} \approx 1.1$ for $C = 2.2 \times 10^{-2}$ at 323 K, and $C_{\perp} \approx 1.0$ for $C = 3.5 \times 10^{-2}$ at 363 K, i.e., an HLSAD of about PdH composition.

As was shown above, the value of $n_{H\perp}$ for heavily cold-worked specimens [16] is ~ 7 if ρ_{\perp} is taken as 9×10^{15} m⁻² [17]. Using the value of $d_{\perp} \approx 1.3 \times 10^{-9}$ m gives the characteristic values $\eta_{\perp} \approx 0.15$, $\Delta S_b/R \approx -1.7$, $C_{\perp} \approx 0.33$ for $C = 6.8 \times 10^{-3}$ at 273 K and $C = 9.6 \times 10^{-3}$ at 323 K; the average composition of the NDSRs (HLSADs) is close to Pd_3H .

Thus, the largest content of hydrogen trapped by the dislocations (in the HLSADs) both in the cold-rolled (to

78%) and heavily cold-worked specimens [16] is about 0.5 at.% (of the total number of Pd atoms in the specimens), at the largest values of the lattice hydrogen concentration (for the cold-rolled specimens, $C = 1.5 \times 10^{-2}$ at 310 K, $C = 2.2 \times 10^{-2}$ at 323 K, $C = 3.5 \times 10^{-2}$ at 363 K; for the heavily cold-worked ones, $C = 7 \times 10^{-3}$ at 273 K, $C = 1 \times 10^{-2}$ at 323 K).

4. Influence of the segregation atmospheres at dislocations on the apparent characteristics of hydrogen diffusion in a metal (Pd)

In the local-equilibrium approximation for the processes of hydrogen redistribution, the apparent coefficient of the chemical or tracer diffusion of hydrogen D_Σ in a metal (Pd) with a dislocation density ρ_\perp is written as [14, 15]

$$D_\Sigma = \frac{D + D_\perp \eta_\perp (\partial C_\perp / \partial C)}{1 + \eta_\perp (\partial C_\perp / \partial C)}, \quad (11)$$

where D_\perp and D are the coefficients of the chemical or tracer diffusion of hydrogen in the NDSRs (HLSADs) and in the metal lattice without hydrogen traps, respectively; and $\eta_\perp \ll 1$.

On the basis of the analysis of the data of [16] (Section 3 of this paper), one can suppose that in many cases the thermodynamic factors ($f_H \approx 1$, $f_{\perp H} \approx 1$) are close to unity. This means that the coefficients of the chemical and tracer diffusion of hydrogen in the palladium lattice [or in the NDSR (HLSAD)] may have close values.

The first term in the right-hand side of Eqn (11) corresponds to the so-called diffusion-with-trapping effect [30], and the second term corresponds to the effect of diffusion along the segregation regions at dislocations (the NDSR or HLSAD) [30]

In order to show the legitimacy and relative generality of Eqn (11), it is expedient to consider the different extreme situations, including the well-known models.

Situation 1. In the case of approaching the complete (extreme) filling of the trap regions by the diffusant (hydrogen), the quantity $\partial C_\perp / \partial C$ obviously tends to zero. Then, from Eqn (11) it follows that $D_\Sigma \approx D$, i.e., neither the diffusion-with-trapping effect nor the effect of diffusion along the NDSR (HLSAD) is present. Such a situation can be described by the use of the Langmuir absorption isotherm (a Fermi–Dirac type distribution [22]) or the Fowler–Guggenheim one [11, 12, 23]. In this connection, it ought to be emphasized, that in a number of works, for instance [2, 6, 31, 32], a somewhat inadequate concept is used. In these works it is proposed (without convincing grounds) that in the case of nearly complete filling of the dislocation traps of hydrogen, only the second term disappears in the equation of type (11), i.e., a diffusion-with-trapping effect takes place. A critical analysis of such an ambiguous concept [31] is presented in [15].

Situation 2. In the case of implementation of a Boltzmann-type or Henry-isotherm-type distribution law [i.e., Eqn (8) if the quantities ΔH_b , ΔS_b do not depend on the hydrogen content in the material], a simple relationship holds:

$$\frac{\partial C_\perp}{\partial C} = K_\perp, \quad (8')$$

where K_\perp is a positive constant quantity. Such a simple situation [Eqn (8')] can be, in particular, related to the case

of the NDSRs (HLSADs) with a compound-like (hydride-like) structure of variable composition. The effective distribution law in this case can be approximated to a linear form [Eqns (6, 8)] within a limited concentration range [11, 25]; the effective binding enthalpy can be close to the dissolution enthalpy of the compound (hydride) in the metal [11, 25]. Then, the following equation is obtained from (11) and (8'):

$$D_\Sigma \approx \frac{D + \eta_\perp K_\perp D_\perp}{1 + \eta_\perp K_\perp}; \quad (11')$$

the first term on the right-hand side of Eqn (11') coincides with the widely used Oriani relation [2]. Equation (11') is in accordance with equation (5.28) from [33] for the multi-channel diffusion with reversible exchange. However, in [33] it is not taken into account that for a more general case an equation of type (11) ought to be used.

From Eqns (11') and (6), one can obtain a rather important unconventional equation [14, 15]

$$D_\perp \approx \frac{D_\Sigma C_\Sigma - DC}{C_\Sigma - C}, \quad (12)$$

which allows one to evaluate the diffusion coefficient for the segregation regions at dislocations (NDSR, HLSAD) from the data corresponding to the so-called regime A of grain-boundary diffusion [32].

Situation 2.1. For the case of $\eta_\perp K_\perp \ll 1$, i.e., when the majority of the diffusant atoms are located in the normal (without defects and stresses) lattice of the metal (Pd), one can obtain from (11') the following well-known relation:

$$D_\Sigma \approx D + \eta_\perp K_\perp D_\perp, \quad (11'')$$

corresponding to the Hart relation (if $K_\perp = 1$) or the Hart–Mortlock one [34] (if $K_\perp > 1$).

Situation 2.2. For the case of $\eta_\perp K_\perp \gg 1$, i.e., when the majority of the diffusant is localized in the NDSR (HLSAD), Eqn (11') becomes

$$D_\Sigma \approx \frac{D}{\eta_\perp K_\perp} + D_\perp. \quad (11''')$$

For the case under consideration ($\eta_\perp K_\perp \gg 1$), the apparent solubility is approximated as

$$C_\Sigma \approx C \eta_\perp K_\perp \approx A \exp \left(-\frac{\Delta H_\Sigma}{RT} \right), \quad (6')$$

where ΔH_Σ is the apparent enthalpy of dissolution of hydrogen in metal (Pd); $C \approx \theta$; A is a positive constant quantity; from Eqns (3), (8) and (6'), it follows that $\Delta H_\Sigma = \Delta H_H^0 + 2W_{H-H}\theta - \Delta H_b$.

Situation 2.2.1. It follows from Eqns (11''') and (12) that $D_\Sigma \approx D_\perp = D_{0\perp} \exp(-Q_\perp/RT)$ if the first term of the sum is much less than the second one ($D/(\eta_\perp K_\perp) \ll D_\perp$), i.e., if the NDSR (HLSAD) are the 'fast diffusion paths,' in comparison with the volume diffusion-with-trapping. In this case, the apparent activation enthalpy of diffusion coincides with the activation enthalpy of hydrogen diffusion in the NDSR or HLSAD ($Q_\Sigma = Q_\perp$), and the preexponential factor of the apparent diffusion coefficient coincides with the factor of the diffusion coefficient of hydrogen in the NDSR or HLSAD ($D_{0\Sigma} = D_{0\perp}$). In this case, the apparent diffusion coefficient of hydrogen in α palladium (with a relatively low hydrogen

content) may be close to the diffusion coefficient of hydrogen in the hydride-like segregation structure (HLSAD) of the type of the β -Pd phase; the diffusion transport of hydrogen through the metal (Pd) corresponds to ‘regime A’ in terms of grain-boundary diffusion [32]. In other words, in this case both hydrogen diffusion and hydrogen solubility are mainly localized in the NDSRs (HLSADs).

Analysis of the experimental data [6, 32] has shown that such a situation can hold for diffusion and solubility of hydrogen in nanocrystalline metals, but with respect to the grain boundaries.

Situation 2.2.2. From equations (11''') and (8) it follows that if $D/(\eta_{\perp}K_{\perp}) \gg D_{\perp}$, then $D_{\Sigma} \approx D/(\eta_{\perp}K_{\perp})D_{0\Sigma} \times \exp(-Q_{\Sigma}/RT)$, $D_{0\Sigma} \approx D_0/[\eta_{\perp} \exp(-\Delta S_b/R)]$, and $Q_{\Sigma} \approx Q + \Delta H_b$, where D_0 and Q are the preexponential factor of the diffusion coefficient and the activation enthalpy of hydrogen diffusion in palladium lattice without dislocations, respectively.

The analysis of the data of [6, 18, 21] presented below (Sections 5 and 6) shows that situations 2.2.1 and/or 2.2.2 could occur in experiments.

5. Re-treatment of the data of [6, 18] on hydrogen solubility, electrical resistance and diffusivity in palladium

In Figs 3–8 of [18], results are presented on a study, by the use of the electrochemical technique, hydrogen solubility and chemical diffusion coefficients (at 295 K and 322 K) in deformed (cold rolled to $\varepsilon = 73, 50, 15$ and 6%) and annealed palladium specimens, over a wide range of hydrogen contents ($C_{\Sigma} = 1 \times 10^{-6} - 7 \times 10^{-3}$).

As has been found [18], the ratio of the apparent solubility of hydrogen (at 295 K) in the deformed ($\varepsilon = 73\%$) specimens to its solubility in the annealed ones (C_{Σ}/C) reaches a value of the order of 1×10^6 for the smallest total concentrations ($C_{\Sigma} = 1 \times 10^{-6}$). For the largest total concentrations $C_{\Sigma} \approx 5 \times 10^{-3}$, this ratio does not exceed 1.3 (Fig. 10 from [18]), which is in satisfactory agreement with the data of [16]. The analysis [19] of the data of [18] carried out in the framework of the theory of dislocations [22] has shown that the apparent binding energy (enthalpy) of hydrogen with dislocations contains a prevailing component ($\Delta H_b \approx 18 \text{ kJ mol}^{-1}$, which is due to the formation of the HLSADs of the type of Pd_2H , with a diameter of about 2.5 nm) at $\rho_{\perp} \approx 8 \times 10^{14} \text{ m}^{-2}$ and $C_{\Sigma} \approx 5 \times 10^{-3}$. In other words, it has been shown [19] that the hydrogen segregates at dislocations in palladium can represent a specific phase, i.e., the material can be considered to be a two-phase system. Note that the results [19] of an analysis of the data of [18] are in satisfactory agreement with the results of the analysis (re-treatment) of the data of [16] presented in Section 3 of this paper.

At the same time, the analysis and interpretation of the diffusion data carried out in [6, 18] seems ambiguous with respect to the following aspects: the definition of the coefficient of the thermodynamic activity of the lattice hydrogen (as $\gamma = C_{\Sigma}/C$) and, as its consequence, the definition of the thermodynamic factor of the chemical diffusion coefficient of the lattice hydrogen [as $f_H = (C/C_{\Sigma})\partial C_{\Sigma}/\partial C$]; the expressions used for the coefficients of the chemical and tracer diffusions of the lattice hydrogen; the acceptability of the Oriani model [2] for the data of [6, 18]; the absence of a consideration of the coefficient of thermodynamic activity (γ_{\perp}), the thermodynamic factor ($f_{\perp H}$), and the coefficients of

the chemical and tracer diffusion of hydrogen for the second phase, i.e., the NDSR (HLSAD). It may be added that in the framework of the model used in [19], the hydrogen segregation atmospheres at dislocations influence the chemical diffusion coefficient of the lattice hydrogen mainly through the thermodynamic factor f_H , and, consequently, they do not influence the tracer diffusion coefficient; but this contradicts the experimental data [21] on the tracer diffusion.

In this connection, it seems expedient to perform the following: (1) to analyze and interpret the data of [18] on hydrogen solubility in deformed and annealed palladium; (2) to analyze and interpret the data of [6] on the hydrogen contribution to the electrical resistance in deformed palladium, in comparison with the results of analysis of the solubility data [18]; (3) to analyze and interpret the data of [18] on the chemical diffusion coefficient of hydrogen in deformed and annealed palladium using the analysis results on the solubility and resistance [18, 6] (Sections 5.1–5.3), and also the data [21] on the tracer diffusion coefficient (Section 6).

5.1 Analysis and interpretation of the data of [18] on the hydrogen solubility in deformed and annealed palladium

The data (Figs 3–6 in [18]) on the concentration dependence of the electromotive force (emf) ΔE at 295 and 322 K for the annealed Pd specimens with hydrogen contents $C_{\Sigma} \approx 10^{-5} - 10^{-3}$ are satisfactorily described by the Nernst equation for infinitely dilute (ideal) solutions: $\Delta E = (RT/F) \ln C$, where F is the Faraday constant. For real solutions, the concentration of the lattice hydrogen (in the Nernst equation) is replaced by the thermodynamic activity of the lattice hydrogen ($a_H = \gamma C$). Hence, it follows, that the coefficient of the thermodynamic activity of the lattice hydrogen is close to unity ($\gamma \approx 1$), and that $C_{\Sigma} \approx C \approx \theta$. The small deviations from such a dependence for the hydrogen contents $C_{\Sigma} \approx (1 - 10) \times 10^{-3}$ (Fig. 3 in [18]) are obviously caused by the mutual interaction of the dissolved hydrogen atoms. These deviations are satisfactorily described by expression (3), with the characteristics obtained upon the analysis of the data of [16] (see Section 3), according to which $\gamma \approx 0.85$ for $C = 1 \times 10^{-2}$ at 323 K.

The considerable deviations from such a dependence for $C_{\Sigma} \approx (1 - 10) \times 10^{-6}$ (Fig. 3 in [18]) are obviously caused by absorption of the dissolved hydrogen by traps (dislocations and others), since, for such low dilutions, γ is undoubtedly equal to unity. Therefore, the concentration of the lattice hydrogen (C) for the given values of the emf and C_{Σ} , for instance, for $\Delta E = 100 \text{ mV}$ and $C_{\Sigma} = 1.6 \times 10^{-6}$ (Fig. 3 in [18]), can be found by extrapolating the concentration dependence of ΔE for infinitely dilute solutions (the straight line in Fig. 3 of [18]) to the intersection with the horizontal line from the given ΔE value (on the emf axis) and projecting the intersection point onto the concentration axis.

Note that the thus found value of C corresponds to the hydrogen solubility in the annealed palladium that is in equilibrium with the deformed palladium, i.e., for the same value of the chemical potential (and the thermodynamic activity) of the lattice hydrogen. This results in $C \approx 2.6 \times 10^{-7}$ for $C_{\Sigma} \approx 1.6 \times 10^{-6}$ at 295 K. Then, using expressions (6)–(8) gives $(C_{\Sigma} - C)/C \approx \eta_{\perp} K_{\perp} \approx \eta_{\perp} \exp(\Delta H_b/RT) \approx 5$.

According to the evaluations of the authors themselves [18], the dislocation density in the annealed (at 773 K) specimens is about 70 times less than in the deformed ($\varepsilon = 73\%$) ones. Assuming that the dislocation density is

$\rho_{\perp} \approx 2.8 \times 10^{15} \text{ m}^{-2}$ in the deformed ($\varepsilon = 73\%$) specimens [27] and $\rho_{\perp} \approx 4 \times 10^{13} \text{ m}^{-2}$ (i.e., smaller by a factor of 70) in the annealed ones [8], and also using the newly obtained (in Section 3, upon the re-treatment of the data of [16]) value of $d_{\perp} \approx 1.3 \text{ nm}$, we obtain the following values of the characteristics for the annealed specimens [18]: $\eta_{\perp} \approx 6.8 \times 10^{-5}$; $\Delta H_b \approx 27.5 \text{ kJ mol}^{-1}$; $n_{H\perp} \approx (C_{\Sigma} - C)/(b^2 \rho_{\perp}) \approx 0.44$; and $C_{\perp} \approx n_{H\perp} b^2 / d_{\perp}^2 \approx 0.02$.

The obtained values of the trap characteristics for the annealed specimens [18] with 'old' dislocations, i.e., dislocations decorated (upon the annealing) by different impurities (including hydrogen), somewhat differ from the values presented below (see Table 2) of the analogous characteristics for the deformed specimens [18] with close hydrogen contents (C_{Σ}), but with 'new' dislocations, which are not decorated by impurities other than hydrogen. This question has been studied in the [9, 10] for α -iron using the technique of positron annihilation (together with some other techniques).

For the deformed specimens [18], the concentration dependence of the emf (ΔE) for the largest total contents of hydrogen ($C_{\Sigma} \approx (1 - 7) \times 10^{-3}$) is close to the dependence for infinitely dilute solutions (see the straight lines in Figs 4–6 in [18]), with the deduction of a relatively small constituent of the NDSR (HLSAD), which is in accordance with the results of analysis of the data of [16] (see Section 3). It proves that the coefficient of the thermodynamic activity of the lattice hydrogen is close to unity ($\gamma \approx 1$) for all total concentrations under consideration. Therefore, one may suppose that the large deviations from the ideal solution for the lower (and especially, for the smallest) total concentrations ($C_{\Sigma} \approx (1 - 100) \times 10^{-6}$) in the deformed Pd specimens (see Figs 4–6 in [18]) are caused by the dislocation-type hydrogen traps (NDSRs, HLSADs). Then, for the deformed specimens [18] the values of the concentration of the lattice hydrogen (C) and the trap characteristics ($\eta_{\perp} K_{\perp}$, ΔH_b , $n_{H\perp}$, C_{\perp}) for the given values of ΔE and C_{Σ} can be obtained in the above-described way (with respect to the annealed specimens [18]); the results of such a treatment are presented in Tables 1 and 2.

Table 1. Results of re-treatment of the data (Fig. 5 in [18]) on the hydrogen solubility at 295 K in 59–73%-deformed (C_{Σ} , experimental) and annealed (C , evaluated) palladium for the same thermodynamic activity of the lattice hydrogen.

$C_{\Sigma} \times 10^4$	8.1	13	65
$C \times 10^4$	5.6	10	49
$(C_{\Sigma} - C)/C = \eta_{\perp} K_{\perp}$	0.45	0.30	0.33

Table 2. Results of re-treatment of the data (Fig. 6 in [18]) on the hydrogen solubility at 322 K in 50%-deformed (C_{Σ} , experimental) and annealed (C , evaluated) palladium for the same thermodynamic activity of the lattice hydrogen.

$C_{\Sigma} \times 10^5$	$C \times 10^5$	$(C_{\Sigma} - C)/C$	$\Delta(C_{\Sigma} - C)/\Delta C$	$(C_{\Sigma} - C)/(b^2 \rho_{\perp})$	$C_{\perp} \times 10^3$
0.7	0.001	700		0.05	2
1.0	0.004	250	100	0.07	3
1.4	0.015	92	36	0.09	4
2.5	0.15	16	7.1	0.16	7
4.8	0.8	5.0	2.5	0.27	12
8.3	2.4	2.5	1.2	0.40	18
16	7.2	1.2	0.6	0.60	26
31	16	0.94	0.7	1.0	45
61	42	0.45	0.7	1.3	57
170	130	0.31	0.2	2.7	120
690	560	0.23	0.2	8.6	380

From the results of treatment of the data of [16] (Section 3), one can obtain for the Pd specimens deformed to 78% $\eta_{\perp} K_{\perp} \approx 0.42$ (at 295 K), which is in satisfactory accord with the values presented in Table 1 for the 73%-deformed Pd specimens [18], for the close total hydrogen contents C_{Σ} . This also follows from the comparison of the data of different works presented in Fig. 10 in [18].

The values presented in Table 2 for $(C_{\Sigma} - C)/(b^2 \rho_{\perp}) \approx n_{H\perp}$, Eqn (9), correspond to $\rho_{\perp} \approx 2 \times 10^{15} \text{ m}^{-2}$ [27]; the local hydrogen concentration in the NDSRs (HLSADs) has been evaluated by the equation

$$C_{\perp} \approx \frac{n_{H\perp} b^2}{d_{\perp}^2}; \quad (13)$$

where d_{\perp} is assumed to be equal to 1.3 nm (as for the 78%-deformed specimens [16]). The C_{\perp} values presented in Table 2 (for the above-mentioned values of ρ_{\perp} and d_{\perp}) show that the HLSADs, within the whole volume of the near-dislocation segregation regions (NDSRs), can only occur for high enough total contents of hydrogen ($C_{\Sigma} \approx 7 \times 10^{-3}$). A similar situation also occurs when using the values $\rho_{\perp} \approx (6.4 - 7.7) \times 10^{14} \text{ m}^{-2}$ and $d_{\perp} \approx 2.5 \text{ nm}$, as is assumed in [19].

Analogous results can be obtained by such a treatment of the data on the hydrogen solubility at 295 K in the 50–73%-deformed palladium (Fig. 4 of [18]).

On the other hand, a comparison of the results given in Table 2 and Table 3 (the latter is presented in Section 5.2) suggests that at low total contents of hydrogen (when the evaluated values of C_{\perp} (Table 2) are rather far from the hydride-like local concentrations), an 'island-like' distribution of the segregation hydride-like nanophases at dislocations can arise. In other words, a partial filling of the NDSR volume by some specific isolated nanoprecipitates can occur, which is in accordance with the concept of local clustering.

By using Eqns (6), (8), and (8'), from the temperature and concentration dependences of $(C_{\Sigma} - C)/C$ and $\Delta(C_{\Sigma} - C)/\Delta C$ (Tables 1, 2 of the present paper; Figs 4–6 of [18]), one can also evaluate the other characteristics of the traps (NDSRs, HLSADs) for different total contents C_{Σ} : ΔH_b , K_{\perp} (in the approximation of $\Delta S_b \approx 0$), η_{\perp} . For a number of cases, this results in reasonable values of $\Delta H_b \approx 40 - 20 \text{ kJ mol}^{-1}$ and, correspondingly, reasonable values of K_{\perp} (increasing with reduction of C_{Σ}). But this also results in considerably overestimated values of η_{\perp} , pointing out the necessity of a definite modification of both the experimental data and their treatment.

At the same time, it should again be noted that the comparison of the analysis results (Tables 1–3) shows the possibility of an island-like distribution of the segregation hydride-like nanophases at dislocations in deformed palladium at low total contents of hydrogen. This may explain the high values obtained for $\eta_{\perp} K_{\perp}$ and ΔH_b for low values of C_{Σ} , $n_{H\perp}$ and C_{\perp} (see Table 2).

Note also that the above values obtained for the traps' characteristics are used in the interpretation of the data of [6] and [18, 21] in the next sections.

5.2 Analysis and interpretation of the data of [6] on the hydrogen contribution to the electrical resistance of deformed palladium

In [6] (in Fig. 31), data are presented on the concentration dependence (at 300 K) of the ratio of the derivative of the electrical resistivity with respect to the total hydrogen

concentration for the deformed (to $\varepsilon = 15, 50, 90, 99\%$) palladium ($\partial\rho_e/\partial C_\Sigma$) to the derivative of the electrical resistivity with respect to the lattice hydrogen concentration for the annealed palladium ($\partial\rho/\partial C$). Some of these data are presented in Table 3.

Table 3. Data (from Fig. 31 [6]) on the concentration (C_Σ) dependence of the ratio $(\partial\rho_e/\partial C_\Sigma)/(\partial\rho/\partial C) = \chi$ at 300 K for the 50%-deformed (ρ_e) and annealed (ρ) palladium specimens

$C_\Sigma \times 10^4$	0.1–0.6	1.0	2.0	4.0	6.0	8.0	10	14	21	30	51	71	92
$\chi \times 10^1$	≤ 0.1	0.8	2.8	4.9	6.0	6.7	7.1	7.8	8.3	8.8	9.4	9.5	9.6

If the hydrogen concentration is expressed in atomic percent, then the quantity $\partial\rho/\partial C = \rho_H$ characterizes the contribution of 1 at.% lattice hydrogen to the electrical resistivity of annealed palladium (without hydrogen traps), and the quantity $\partial\rho_e/\partial C_\Sigma = \rho_{sH}$ is the contribution of 1 at.% total hydrogen in deformed palladium (with hydrogen traps). Hence, we obtain the expression:

$$\chi = \frac{\rho_{sH}}{\rho_H} = \frac{\rho_{sH}}{\rho_H} \left(\frac{C_\Sigma - C}{C_\Sigma} \right) + \frac{C}{C_\Sigma}, \quad (14)$$

where ρ_{sH} is the corresponding (scattering effect) contribution of 1 at.% hydrogen localized in NDSRs (HLSADs); and $(C_\Sigma - C)/C_\Sigma$ is the fraction of the total hydrogen localized in the NDSRs (HLSADs).

As is seen from Table 3, for the deformed ($\varepsilon = 50\%$) specimens with a hydrogen total content $C_\Sigma \approx (1 - 6) \times 10^{-5}$, the value of χ is about zero (within the uncertainty limits, ≤ 0.01). According to equation (14), this means that for such total contents of hydrogen the following relationships are fulfilled: $\rho_{sH}/\rho_H \leq 0.01$, $C/C_\Sigma \leq 0.01$; in other words, (i) the major part of the total hydrogen is localized in NDSRs (HLSADs), and (ii) ρ_{sH} is negligible in comparison with ρ_H (as is expected for a hydride phase [6]). By substituting the data on C and C_Σ for the deformed ($\varepsilon = 50\%$) specimens (from Tables 1, 2) into Eqn (14), as well as the data on χ (from Table 3), we obtain $\rho_{sH} \approx 0$ for the contents up to $C_\Sigma \approx 1.3 \times 10^{-3}$; in this case, $\chi \approx C/C_\Sigma$. The analysis also shows the necessity of some correction of the data, probably, due to the different sensitivity of the two techniques used.

At the same time, for higher total hydrogen contents, a value of ρ_{sH} is obtained close to ρ_H . For instance, for $C_\Sigma \approx 5.6 \times 10^{-3}$, C/C_Σ is about 0.75 (Table 2), and χ is about 0.94 (Table 3); hence, by using Eqn (14), we obtain $\rho_{sH}/\rho_H \approx 0.8$. For $C_\Sigma = 1.0 \times 10^{-2}$, according to the data of [16] presented in Section 3 for $\varepsilon = 78\%$, C/C_Σ is about 0.72, and according to the data shown in [6, Fig. 31], χ is about 0.92; hence, $\rho_{sH}/\rho_H \approx 0.7$.

The results of the analysis (re-treatment) presented above (in Sections 5.1, 5.2) of the data on the solubility [18] and the electrical resistance [6] allow one to make the following conclusions.

(1) At total hydrogen contents $C_\Sigma \approx (1 - 100) \times 10^{-6}$, the prevailing fraction of the total hydrogen in the deformed ($\varepsilon = 50 - 90\%$) palladium ($(C_\Sigma - C)/C_\Sigma$) at 300–320 K is localized in the hydride-like segregation nanophases (nanoprecipitates) at dislocations or in dislocation atmospheres. These segregates at dislocations are characterized by a negligible contribution to the electrical resistance (which is typical for ordered stoichiometric hydrides), by relatively high values of the enthalpy of binding with dislocations (increasing with reduction of C_Σ), by an effective diameter

of the segregation atmospheres (regions) less than 1 nm, and by an ‘island-like’ distribution of the segregation nanophases in the NDSRs (at low C_Σ).

(2) At $C_\Sigma \approx 1 \times 10^{-2}$, a prevailing or considerable fraction of the total hydrogen (C/C_Σ) in the deformed ($\varepsilon = 50 - 80\%$) palladium at 300–320 K dissolves in the normal lattice of the metal; the rest of the hydrogen (about 10–50% of C_Σ) is localized in the NDSRs (HLSADs). The segregates at dislocations are characterized by a hydride-like composition in the whole volume of the NDSR, by an effective diameter on the order of a few nm, by lower values of the enthalpy of binding with dislocations, by an apparent distribution law of the Boltzmann type, and also by a considerable contribution to the electrical resistance, which is close to that for lattice hydrogen (which is typical of a cluster-type disordered hydride structure of variable composition).

5.3 Analysis and interpretation of the data of [18] on the chemical diffusion coefficient of hydrogen in deformed and annealed palladium

The data obtained by the use of the pulse and potentiostatic techniques (Fig. 8 in [18]) on the concentration (C_Σ) dependence and magnitudes of the chemical diffusion coefficients at 322 K for hydrogen in deformed ($\varepsilon = 50\%$, 73%) and annealed palladium (with $C_\Sigma \approx (5 - 260) \times 10^{-5}$) are satisfactorily described by Eqn (11) (see Table 4).

Table 4. Results of treatment [using Eqn (11), for the case of $D \gg D_\perp \eta_\perp (\partial C_\perp / \partial C)$] of the data of Fig. 8 in [18] on the chemical diffusion coefficient of hydrogen at 322 K obtained using the pulse technique for Pd deformed to 50% (D_Σ) and for annealed palladium (D) [with $C_\Sigma = (5 - 260) \times 10^{-5}$].

$C_\Sigma \times 10^5$	4.9	8.5	15.5	32	66	150	260
$(D/D_\Sigma) - 1 = \eta_\perp \partial C_\perp / \partial C$	1.6	0.8	0.6	0.3	0.3	0.21	0.12

The values obtained (from the diffusion data of [18]) for $\eta_\perp (\partial C_\perp / \partial C)$ (see Table 4) are satisfactorily agree with the values (obtained from the solubility data of [18]) of $\Delta(C_\Sigma - C)/\Delta C \approx \eta_\perp (\partial C_\perp / \partial C)$ and $(C_\Sigma - C)/C$ (see Table 2) at the same hydrogen contents C_Σ . This shows the validity of the model used [Eqn (11)].

For lower hydrogen contents ($C_\Sigma \approx (3 - 40) \times 10^{-6}$) in the same deformed ($\varepsilon = 50\%$, 73%) specimens (see Fig. 8 in [18]), the character of the concentration dependence of the apparent diffusion coefficient (D_Σ) changes at 322 K, tending to saturation, i.e., to some constant value ($D_{\Sigma s} \approx 2.3 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$) for the lowest C_Σ . By using the data from Tables 2 and 3, one can show that in the given case situation 2.2.1 is realized (Section 4), i.e., $D_{\Sigma s} \approx D_\perp$, where D_\perp is the diffusion coefficient of hydrogen in the NDSRs (HLSADs). Really, according to the data from Tables 2 and 3, for $C_\Sigma \approx (3 - 40) \times 10^{-6}$ in the deformed ($\varepsilon = 50 - 73\%$) specimens, at 322 K, most part of hydrogen is localized in the NDSRs (HLSADs). In this case, the apparent coefficient of hydrogen diffusion-with-trapping in the deformed palladium, with reversible capture of the diffusant by the traps (that is, $D/[1 + \eta_\perp (\partial C_\perp / \partial C)]$, where $D \approx 7.3 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ is the hydrogen diffusion coefficient at 322 K in the annealed specimens [18], and $\eta_\perp (\partial C_\perp / \partial C) \approx \Delta(C_\Sigma - C)/\Delta C$ is taken from Table 2) is obtained at a considerably lower $D_{\Sigma s}$ than the experimental value. This shows that the conditions of situation 2.2.1 are realized.

Table 5. Results of re-treating the data given in Figs 6 and 7 in [21] on the diffusion coefficients of tritium, at different T in deformed (D_{Σ}) and annealed (D) palladium (with $C_{\Sigma} \approx 10^{-5}$) using Eqn (11') for the case of $D \gg \eta_{\perp} K_{\perp} D_{\perp}$, i.e., for variant I of the data treatment.

ε , %	ΔH_b , kJ mol $^{-1}$	$\eta_{\perp} \exp(-\Delta S_b/R)$	$\eta_{\perp} K_{\perp}$ at different temperatures				
			283 K	293 K	303 K	313 K	323 K
76	15.0 \pm 0.6	4.4 $\times 10^{-3}$	2.6	2.1	1.7	1.4	1.2
56	16.0 \pm 0.9	2.3 $\times 10^{-3}$	2.1	1.6	1.3	1.1	0.9
35	17.3 \pm 1.5	1.8 $\times 10^{-3}$	1.6	1.3	1.0	0.8	0.6
30	19.1 \pm 1.5	3.9 $\times 10^{-4}$	1.3	1.0	0.8	0.6	0.5

Close results can be obtained from the diffusion data for the deformed ($\varepsilon = 73\%$, 15%) specimens at 295 K (Fig. 7 of [18]); this results in a value of $D_{\Sigma s} \approx D_{\perp} \approx 5.0 \times 10^{-12}$ m 2 s $^{-1}$. By using the values of $D_{\Sigma s}$ (i.e., D_{\perp}) obtained for the two temperatures, one can evaluate the corresponding activation enthalpy $Q_{\perp} \approx 45$ kJ mol $^{-1}$ and the preexponential factor of the hydrogen diffusion coefficient for NDSRs (HLSADs) $D_{0\perp} \approx 4 \times 10^{-4}$ m 2 s $^{-1}$, which agree with the known data on hydrogen diffusion in the β phase (Pd $_2$ H) [35].

Some differences in the concentration dependence and values of D_{Σ} for the lowest C_{Σ} (when nearing $D_{\Sigma s}$) obtained using two different techniques (Figs 7 and 8 in [18]) can be related to the difference in the hydrogen distribution and in the average values of the hydrogen content in the specimens under the techniques' conditions [18], and also to possible changes in the island-like structure of the HLSADs.

The values and the concentration dependence of the chemical diffusion coefficients of hydrogen at 295–322 K in the deformed to 16–73% (D_{Σ}) and annealed (D) palladium with $C_{\Sigma} \approx 10^{-6}$ – 10^{-3} [18] satisfactorily agree with the data [21] on the tracer diffusion coefficients of hydrogen at 283–323 K in the deformed to ($\varepsilon = 13$ –76%) and annealed palladium with $C_{\Sigma} \approx 10^{-5}$ – 4×10^{-4} . This points to the closeness [30] of the thermodynamic factor of the chemical diffusion coefficient to unity and to the acceptability of the same model (the situation 2.2.1 in Section 4) in the case of the tracer diffusion (see the next section).

6. Re-treatment and interpretation of the data of [21] on the tracer diffusion coefficient of hydrogen in deformed and annealed palladium

In Ref. [21], data are presented on the tracer diffusion coefficient of hydrogen at 283–323 K in cold-rolled Pd specimens with different degrees of plastic deformation ($\varepsilon = 13$ –76%) and in annealed Pd specimens, obtained using tritium isotopes. In one set of experiments [21], the temperature dependence of the diffusivity was studied at very low tritium-to-metal ratios ($C_{\Sigma} \leq 10^{-5}$). Within the Oriani approximation [2], and using the Henry-isotherm formulae, the enthalpy of tritium binding with traps was obtained to be [21] $\Delta H_b = 18 \pm 3$ kJ mol $^{-1}$. In another set of experiments [21], the influence of precharging with hydrogen (to $C_{\Sigma} \approx 4 \times 10^{-4}$) on the tritium diffusion at 303 K was also studied for specimens deformed to $\varepsilon = 30$ and 50%. By means of a self-consistent consideration of the corresponding experimental data, using the Langmuir isotherm approximation, the binding entropy of tritium with traps (ΔS_b) and the concentration (atomic fraction) of traps (η_{\perp}) were determined [21] to be (a) $\Delta S_b/R = -1.12$, $\eta_{\perp} = 8.12 \times 10^{-5}$ for the samples deformed to 30% (at 303 K); and (b) $\Delta S_b/R = -2.15$, $\eta_{\perp} = 1.62 \times 10^{-4}$ for the 50%-deformed samples (at 303 K). The authors of Ref. [21] suggest that it is the

dislocation cores and their nearest surroundings that serve as the main hydrogen traps.

As the results of the analysis presented below show, such treatment and interpretation of the data of [21] correspond to one (I) of the two possible variants (I and II). The results of the re-treatment of the data of [21] in the framework of the model developed in Section 4 for variant I are presented in Tables 5 and 6.

Table 6. Results of re-treatment of the data of Fig. 4 in [21] on the diffusion coefficient of tritium at 303 K for precharged (to C_{Σ}) deformed (D_{Σ}) and annealed (D) palladium, using Eqn (11), for the case of $D \gg D_{\perp} \eta_{\perp} (\partial C_{\perp} / \partial C)$, i.e., variant I of the data treatment.

$\varepsilon = 30\%$							
$C_{\Sigma} \times 10^5$	≤ 1.0	1.2	2.0	5.0	10	24	
$(D/D_{\Sigma}) - 1$	0.8	0.6	0.6	0.45	0.3	0.2	
$\varepsilon = 50\%$							
$C_{\Sigma} \times 10^5$	≤ 1.0	2.9	5.0	0.5		45	
$(D/D_{\Sigma}) - 1 =$	1.3	0.7	0.7			0.15	
$\eta_{\perp} \partial C_{\perp} / \partial C$							

By assuming, according to [27], that the dislocation densities are $\rho_{\perp} \approx 2.7 \times 10^{15}$ m $^{-2}$ for $\varepsilon = 76\%$, 2.1×10^{15} m $^{-2}$ for $\varepsilon = 56\%$, and 1.5×10^{15} m $^{-2}$ for $\varepsilon = 35\%$, using the values of $\eta_{\perp} \exp(-\Delta S_b/R)$ (Table 5) and $\Delta S_b \approx 0$, we obtain [by the use of Eqn (7)] $d_{\perp} \approx 1.1$ nm. The values of ΔH_b and $\eta_{\perp} \exp(-\Delta S_b/R)$ presented in Table 5 and the value of d_{\perp} for the specimens deformed to 76% [21] are consistent with the values (estimated in Section 3) of the analogous characteristics for the 78%-deformed samples [16], despite the large difference (several orders) in the hydrogen contents C_{Σ} .

The decrease in $\eta_{\perp} (\partial C_{\perp} / \partial C)$ with increasing C_{Σ} shown in Table 6 for the deformed specimens [21] could be interpreted in the framework of the Langmuir isotherm approximation, as the authors of the Ref. [21] did. However, it does not agree with the analysis results of the data of [16, 18] (see Sections 3 and 5.1), according to which, for the deformed ($\varepsilon = 50$ –78%) palladium even with higher total contents of hydrogen (to $C_{\Sigma} \approx 1 \times 10^{-2}$), the effective Boltzmann-type distribution law can be fulfilled (that is, without the Langmuir saturation). Therefore, the above-quoted estimate [21] of η_{\perp} seems to be underestimated.

By using the results of analysis of the data of [16] (Section 3), we obtain for the deformed (78%) specimens ($C_{\Sigma} \approx 3 \times 10^{-4}$ – 1×10^{-2} , $T = 310$ –363 K) at 303 K a value $\eta_{\perp} K_{\perp} \approx \eta_{\perp} (\partial C_{\perp} / \partial C) \approx 0.36$. This value corresponds to $\rho_{\perp} \approx 3 \times 10^{15}$ m $^{-2}$ (for $\varepsilon = 78\%$, according to Ref. [27]). For $\rho_{\perp} \approx 2 \times 10^{15}$ m $^{-2}$, as for specimens deformed to 50% [21] (according to [27]), we obtain a value of 0.24 instead of 0.36, which is in satisfactory agreement with the value 0.15 presented above (Table 6) for the 50%-deformed specimens [21] ($C_{\Sigma} \approx 4.5 \times 10^{-4}$, $T = 303$ K).

The values of $\eta_{\perp}(\partial C_{\perp}/\partial C)$ for $\varepsilon = 50\%$, $C_{\Sigma} \approx 4 \times 10^{-4}$, $T = 303$ K [see Table 6]) also satisfactorily agree with the values [18] extrapolated to the same values of ε , C_{Σ} , and T (see Tables 1, 5).

At the same time, at lower hydrogen contents, the characteristics of the traps $[\eta_{\perp}K_{\perp} = (C_{\Sigma} - C)/C$ and $\eta_{\perp}(\partial C_{\perp}/\partial C) \approx \Delta(C_{\Sigma} - C)/\Delta C \approx \eta_{\perp}K_{\perp}]$ presented in Tables 5 and 6 considerably differ [by up to three–four orders of magnitude for $C_{\Sigma} \leq 1 \times 10^{-5}$ and to one–two orders of magnitude for $C_{\Sigma} \approx (3 - 5) \times 10^{-5}$] from the corresponding characteristics (see Tables 2, 3) obtained from the data of [6, 18] on hydrogen solubility and electrical resistance in palladium for the same values of ε , C_{Σ} , and T as in Ref. [21]).

By using the values of $\Delta(C_{\Sigma} - C)/\Delta C$ (Table 2) for the deformed ($\varepsilon = 50\%$) palladium [18] (with $C_{\Sigma} \approx 1 \times 10^{-5}$) and the D values for the annealed palladium [21], one can evaluate the apparent coefficients of hydrogen diffusion with reversible capture of the diffusant by the traps (that is, $D/[1 + \eta_{\perp}(\partial C_{\perp}/\partial C)]$ that are considerably lower than the experimental values of D_{Σ} for the deformed specimens (Fig. 6 in [21]). This shows that at least for $C_{\Sigma} \leq 1 \times 10^{-5}$ in the deformed ($\varepsilon = 30 - 76\%$) specimens (Figs 3, 6 in [21]), situation 2.2.1 (see Section 4) is realized, i.e., $D_{\Sigma} \approx D_{\perp}$ (variant II of the data treatment).

Therefore, one can believe that the data given in Fig. 3 in [21] characterize tritium diffusion in NDSRs (HLSADs) in the deformed ($\varepsilon = 30 - 76\%$) palladium at 283–323 K and $C_{\Sigma} \leq 1 \times 10^{-5}$. However, the values $Q_{\perp} \approx 27.4$ kJ mol $^{-1}$ and $D_{0\perp} \approx 1.3 \times 10^{-6}$ m 2 s $^{-1}$ are much lower than the values Q_{\perp} and $D_{0\perp}$ obtained in Section 5.3 (from the D_{\perp} values at 322 K and 295 K for the specimens described in [18]).

In this connection, it is relevant to note that the values of the diffusion characteristics obtained in [21] (Fig. 3) for hydrogen in annealed palladium, i.e., $Q \approx 18$ kJ mol $^{-1}$ and $D_0 \approx 1.0 \times 10^{-7}$ m 2 s $^{-1}$, are also lower than those obtained in [18]: $Q \approx 23$ kJ mol $^{-1}$ and $D_0 \approx 4.1 \times 10^{-7}$ m 2 s $^{-1}$. Therefore, by taking into account the measurement errors, one can believe that the results of the analysis of diffusion data given in [18] and [21] may be considered to be in satisfactory agreement.

7. Conclusions

The results of the analysis and re-treatment of a series of the most convincing experimental data on the solubility, electrical resistance, and diffusivity of hydrogen in deformed and annealed palladium prove the possibility of formation of hydride-like segregation atmospheres at dislocations, which is, in particular, confirmed by the data on the small-angle scattering of neutrons.

The structure, composition, diameter (up to several nm), effect on the electrical resistance, thermodynamic and diffusion characteristics of the segregation atmospheres at dislocations in palladium can vary in wide limits depending on the concentration and thermodynamic activity of the lattice hydrogen, that is, hydrogen dissolved in the normal (without defects and stresses) lattice of palladium. Further, the formation of hydride-like segregation nanophases at dislocations in palladium occurs even in the case of large undersaturation of the solid solution with respect to the hydride precipitation in the normal lattice of palladium, i.e., it is expedient to consider a specific phase diagram of the ‘hydrogen–segregation nanoregions at dislocations in palla-

dium’ type, in comparison with the conventional phase diagram of the ‘hydrogen–palladium’ type.

The methodology presented in Sections 2–6 and the results of determination of the characteristics of the hydrogen segregation at dislocations in palladium can be applied for revealing the micromechanisms of hydrogen influence on physical and mechanical properties of palladium and palladium-based alloys and also for optimization of the regimes of thermal-hydrogen treatment and hydrogen-induced transformation hardening of the materials.

The results presented may have a special significance for the description of the influence of dislocations (being introduced by different ways of processing and treatment of palladium and palladium-based alloys) on the total content of hydrogen, its distribution in the materials, and the local states of hydrogen in the segregation nanoregions at dislocations, which goes beyond the framework of the conventional ‘hydrogen–palladium’ phase diagram.

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