

Hydrogen diffusion in disordered metals and alloys

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Abstract. The state of the art of research into the diffusion of hydrogen in metallic systems with chemical and crystalline disorder is reviewed. The physical principles and capabilities of existing experimental methods for studying hydrogen diffusion in equilibrium and nonequilibrium conditions are discussed. The current theoretical understanding of and approaches to the problem are critically analyzed. Based on the authors' original research, a quite general formalism is proposed for describing hydrogen diffusion on disordered media, which allows the analytical solution of the problem and — very importantly — enables diffusion and structural data to be used to identify the structure of amorphous and nanocrystalline alloys.

1. Introduction

This work is devoted to the problem of hydrogen diffusion in disordered metals and alloys. The state of the art in the field of hydrogen storage, hydrogen treatment, and its diffusion in other systems (semiconductors, films, etc.) have been considered in Ref. [1] (see also Refs [1, 2, 8] therein). Among the domestic publications concerning the properties of films of interstitial phases, Ref. [2] can be distinguished, which includes a vast bibliography, and review [3], which considers a wide circle of problems related to the production and properties of hydrogen-containing carbon nanostructures.

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The investigation of hydrogen transport in disordered metallic systems is stimulated by factors of both a technological and a fundamental nature. The technological applications are related to the traditional interest in the metal-hydrogen systems in atomic energetics (use of metal hydrides in structural elements of nuclear reactors [4]), powder metallurgy, and a very wide circle of problems of the so-called 'hydrogen energetics'. In recent years, the last has taken on an ever-growing importance in ecology [5]. The most important of its problems are:

(a) the purification of gaseous hydrogen (palladium alloys with a high permeability for hydrogen, which are applied as membranes [6, 7]);

(b) the storage of hydrogen in the form of metal hydrides [8] (titanium-, zirconium-, and magnesium-based alloys capable of reversibly absorbing large amounts of hydrogen; the nanocrystalline Mg_2Ni alloy should be specially noted, which absorbs much greater amounts of hydrogen at room temperature than its polycrystalline analog does [9]);

(c) the production of electrodes for fuel cells (alloys that recommended themselves as good materials for hydrogen storage, e.g., the Mg_2Ni compound [10]).

For fundamental investigations, it is important that hydrogen in alloys, as the lightest interstitial impurity carrying a single electron, is the simplest object suitable for studying interactions between a solvent and a diffusant. The small activation energy (~ 0.1 eV in pure metals [11]) and a relatively weak effect on structural relaxation permit one to consider hydrogen diffusion as an efficient method for studying the microstructure of amorphous and nanocrystalline alloys [12, 13]. However, to correctly interpret experimental data, it is necessary to develop theoretical *analytical* models of transport in disordered materials with allowance for the specific features of their structure on atomic and mesoscopic levels.

Thus, the task of the theory is to develop adequate models that would permit one to obtain expressions for the diffusion coefficient containing a minimum number of free parameters, since otherwise their determination would require additional experiments.

Hydrogen diffusion in metals and alloys. At present, the most comprehensively studied problem is that of hydrogen diffusion in metals. Numerous experimental and theoretical works have been devoted to this problem (see reviews [11, 14]). The mechanism of the movement of hydrogen atoms reduces to their passage from one interstice to another. In metals with a bcc structure, such transitions occur between tetrahedral interstices (tetrapores), whereas in fcc metals the hydrogen atoms travel over octahedral interstices (octapores).

The specific features of hydrogen diffusion that distinguish it from diffusion of other interstitial atoms, e.g., nitrogen, carbon, oxygen, etc., are, first, the exclusively small activation energy and, second, the quantum character of diffusion, which manifests itself in a wide temperature range up to room temperature.

At ultralow temperatures, only the quantum mechanism of diffusion is possible, which consists in subbarrier quantum tunneling of hydrogen atoms between neighboring interstices. Since the width of the energy band for hydrogen atoms (unlike electrons) is very small, the efficiency of this mechanism is very sensitive to various imperfections in the metal (defects, impurities).

As the temperature increases, the transitions of hydrogen atoms occur with the participation of crystal-lattice vibrations (phonons); these are so-called incoherent transitions. In contrast to the band (coherent) movement of hydrogen, the diffusion coefficient acquires an Arrhenius (activation) dependence on temperature, but the quantum character of the diffusion process continues to manifest itself in unusual isotopic dependences of the prefactor and activation energy. In this regime, diffusion occurs by transitions via excited states of hydrogen atoms (adiabatic thermally activated transitions) or by transitions from one interstice to another in which the hydrogen atom is in the ground state (nonadiabatic transitions, thermally stimulated tunneling). At higher temperatures, the classical mechanism of overbarrier diffusion of atoms is realized, according to which the probability of the transition of an interstitial atom per unit time is

$$\Gamma = \frac{1}{\tau} \exp\left(-\frac{V}{kT}\right), \quad (1.1)$$

where τ^{-1} is the local frequency of vibrations of an interstitial atom and V is the activation energy, equal to the difference between the energy of the hydrogen atom in the saddle point and the potential energy of the hydrogen atom in the interstice. At $kT \geq V$, hydrogen diffusion in metals is similar to diffusion in liquids or gases.

Passing to a more complex process of hydrogen diffusion in alloys, we note that no quantum theory of diffusion in alloys exists at present. However, it should be noted that the role of quantum effects in alloys is much less important than in pure metals. This is due to the fact that the random changes in the potential energy of the proton passing from one interstice into another (which are due to the differences in the atomic surroundings in the alloy) are greater than the width of the proton band (which is proportional to the overlap integral of the proton wave functions in neighboring interstices), so that the purely quantum tunneling becomes impossible. For this reason, we will consider below only the classical regime of diffusion.

The main feature of interstitial diffusion in alloys is that interstices of the same type in the alloy have different configurations of surrounding atoms, which differ in both the number of atoms of various types and the symmetry of

their arrangement [15, 16]. For this reason, the energy of interstitial atoms in various interstices and the activation energies for diffusion will differ from interstice to interstice. Thus, in binary bcc alloys A–B the allowance for the atomic interactions within the first coordination shell (without account for symmetry) yields five configurations for a tetrapore, namely, A_4 , A_3B_1 , A_2B_2 , A_1B_3 , and B_4 . In binary fcc alloys, seven different configurations of octapores exist, namely, A_6 , A_5B_1 , A_4B_2 , A_3B_3 , A_2B_4 , A_1B_5 , and B_6 . In the case of ternary alloys A–B–C, fifteen arrangements with repetitions in four cells for three elements are possible, i.e., 15 different configurations of tetrapores, in the bcc lattice; and 28 arrangements with repetitions in six cells for three elements, i.e., 28 configurations of octapores, in the fcc lattice (without account for the symmetry of the pore surroundings). Therefore, the occupation of interstices will be different; moreover, it will change with temperature T and hydrogen concentration c , which should be taken into account when deriving the expression for the diffusion coefficient of hydrogen. The effect of the finite concentration of diffusing atoms should also be taken into account.

Hydrogen diffusion in amorphous and nanocrystalline materials. In the reviews concerning diffusion in amorphous metallic alloys [18–20] and nanocrystalline materials [21–23], the following features of the behavior of hydrogen in these systems, as opposed to that in crystalline alloys with atomic disorder, are noted. The solubility of hydrogen in amorphous alloys is, as a rule, higher than in polycrystalline samples of the same composition. This is also valid for nanocrystalline materials, and even to a greater extent. Thus, the solubility of hydrogen in nanocrystalline palladium can exceed its solubility in single-crystal palladium by two orders of magnitude [18].

Another important feature is that the diffusion coefficient in systems with crystalline disorder has a stronger dependence on the hydrogen concentration. For example, the coefficient of hydrogen diffusion in Pd- and Ti-based amorphous alloys is somewhat smaller than in crystalline samples, but it increases rapidly with hydrogen concentration and at a certain concentration may exceed the corresponding coefficient for alloys with crystalline disorder [19]. The permeability of samples of nanocrystalline palladium for hydrogen also rapidly increases with increasing hydrogen concentration [18], whereas the coefficient of its diffusion in single-crystal palladium is virtually independent of concentration (Fig. 1).

These features are *qualitatively* explained by the presence of many positions for hydrogen location in disordered materials that differ in energy. As the concentration increases, positions with the lowest energy are first filled, and diffusion occurs over sites with a low activation energy. As the deep potential wells become filled with increasing hydrogen concentration, an increase in the effective coefficient of hydrogen diffusion is observed. The investigation of the spectrum of potential energies of hydrogen atoms in amorphous Ni–Ti and Ni–Zr alloys [24] and in nanocrystalline samples of Pd [18, 25] confirmed the assumption that a quasi-continuous hydrogen energy distribution exists in disordered materials. In nanocrystalline Pd, the spectrum represents a superposition of a delta-like contribution from the bulk of grain lattice and of a bell-shaped contribution from grain boundaries. More interesting data were presented in Ref. [24]. In the crystalline Ni–Zr sample, the energy spectrum of hydrogen atoms is a sum of delta-like contributions corresponding to different types of surroundings

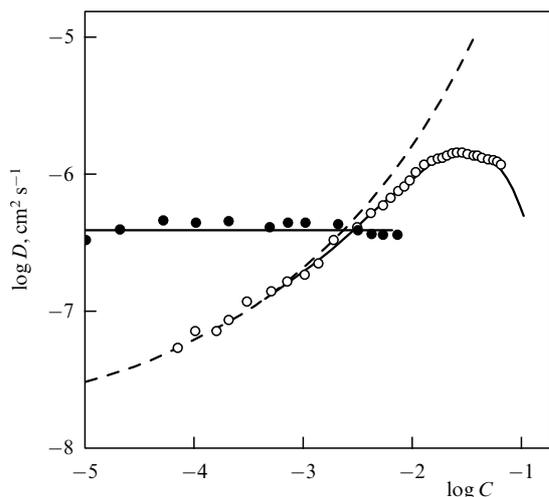


Figure 1. Dependence of the hydrogen diffusion coefficient D in nanocrystalline palladium on hydrogen concentration $C = H/M$ (open circles) [26]. Solid circles show the experimental data for a single-crystal sample of palladium with hydrogen. The decrease in D at $C > 0.03$ is due to the mutual repulsion of protons (see Section 3.4).

formed by Ni and Zr atoms; in the amorphous alloy, bell-shaped curves which partially overlap are observed in place of the delta-like functions, as is shown in Fig. 2. This indicates the presence, in amorphous alloys, of a crystalline short-range order which should noticeably affect the process of hydrogen transport.

Note one more characteristic feature of hydrogen diffusion in amorphous alloys: the temperature behavior of the diffusion coefficient in them deviates from the Arrhenius behavior, as a rule [19]. This may be related to both the dispersion in the energies of their atoms [27] and the dependence of the degree of short-range order in the alloy on its temperature [12]. All this permitted Larikov to conclude [19] that the mass transport in amorphous alloys is in its character closer to diffusion in imperfect crystals than that in liquids. Therefore, we can use the concept of short-range order when describing hydrogen diffusion and call the sites of location of its atoms in amorphous alloys ‘quasi-interstices’

An important feature of nanocrystalline systems is the existence of size effects in them [28, 29], which may be related

to the facts that (a) the grain size and the characteristic lengths of some physical process become close to one another, (b) the role of grain-boundary defects increases on passing to a nanometer scale, and (c) the structure of grain boundaries in nanomaterials differs substantially from that in conventional polycrystals. From this viewpoint, the enhanced capability of absorbing hydrogen by grain boundaries in nanocrystalline palladium and their enhanced permeability for hydrogen are manifestations of size effects (b) and (c). Such behavior is not universal, however. Hirscher et al. [30] investigated fine-scale and large-scale diffusion of hydrogen in nanocrystalline alloys $Fe_{90}Zr_{10}$, $Fe_{60}Co_{30}Zr_{10}$, and $Co_{90}Zr_{10}$ with a grain size of 15–200 nm that were obtained by crystallization from the amorphous state. In the first two alloys, a strong dependence of the diffusion rate on hydrogen concentration was observed, which was explained by the Gaussian distribution of the activation energy in grain-boundary regions; it was also revealed that hydrogen atoms are preferentially located in grain boundaries. In the cobalt-based alloy, on the contrary, the rate of hydrogen transport was independent of its content and hydrogen preferentially concentrated in the bulk of grains. In addition, the diffusive permeability of grain boundaries in this alloy turned out to be very high, and the rate of degassing of the samples on the whole was determined exclusively by the rate with which hydrogen atoms left the volume of individual grains of the material. Note that the experimental investigations devoted directly to studying the role of size effects in hydrogen diffusion are virtually absent. In particular, to the best of our knowledge, there is a single work [31] devoted to the changeover of the regime of hydrogen diffusion in nanocrystalline nickel related to structural relaxation in grain boundaries. The experimental investigations in this case are hindered by the fact that the difference in the mobilities of hydrogen atoms in the bulk of grains and in grain boundaries are usually not so large as in the case of diffusion via the vacancy mechanism [21].

2. Experimental methods of studying hydrogen diffusion

Many physical properties of metals and alloys, such as electrical resistance, rate of hydrogen absorption/desorption, time of mechanical relaxation, magnetic properties, etc., are directly or indirectly related to the content and diffusion coefficient of hydrogen in them. Correspondingly,

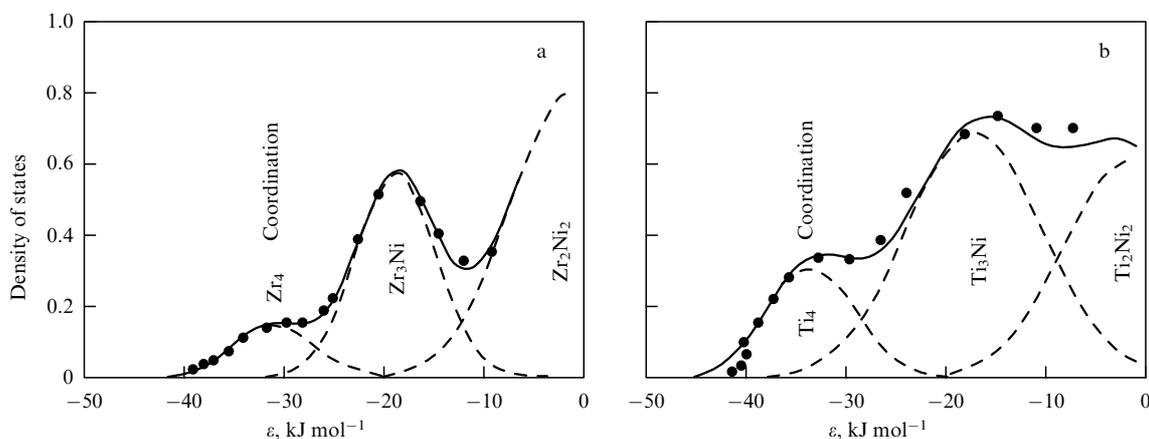


Figure 2. Distribution of potential energies of hydrogen atoms in amorphous alloys (a) Ni–Zr and (b) Ni–Ti according to [24].

the techniques of measuring hydrogen permeability in these substances can be based on various phenomena. Detailed information on the methods of studying hydrogen migration can be found in [11]. The present state of the art of the problem is considered in [32]. In this work, we restrict ourselves to a brief outline of experimental techniques of studying hydrogen diffusion, mainly characterizing their potential and disadvantages.

Hydrogen diffusion is usually studied by creating its nonequilibrium distribution and measuring the rate of its relaxation to the equilibrium state. In addition, special methods exist which permit one to study equilibrium migration of its atoms; these are nuclear magnetic resonance, quasi-elastic neutron scattering, and Mössbauer spectroscopy. In the first case, the characteristic to be measured is the coefficient of chemical diffusion in the empirical Fick's law that relates the flux of impurity atoms with the gradient of its concentration:

$$\mathbf{J} = -D_{\text{ch}} \nabla c. \quad (2.1)$$

In the second case, the coefficient of diffusion of some tracer, or the Einstein diffusion coefficient D_{rw} , which relates root-mean-square displacements of an impurity atom to the time of its motion, is measured:

$$\langle R^2(t) \rangle = 6D_{\text{rw}}t, \quad (2.2)$$

where the average is taken over the ensemble of systems that are under identical macroscopic conditions. At small hydrogen concentrations, when the interaction between its atoms and the effects of blocking of interstices can be completely neglected, these coefficients coincide with one another. At large concentrations, in accordance with nonequilibrium thermodynamics [33], the coefficient D_{ch} is expressed through the mobility of hydrogen atoms \mathcal{M} and the gradient of its chemical potential μ :

$$D_{\text{ch}} = \mathcal{M}c \frac{\partial \mu}{\partial c}. \quad (2.3)$$

At the same time, the tracer diffusion coefficient [1] is written as

$$D_{\text{rw}} = \mathcal{M}kT. \quad (2.4)$$

The last expression is known as the Einstein relation; it was strictly established only for systems with a gas-type disorder and random walk on regular lattices [34]. A comparison of experimental data obtained by various methods thus requires the knowledge of equilibrium characteristics of the metal (alloy)–hydrogen system.

The techniques of the investigation of hydrogen diffusion can be classified according to the methods of production of the nonequilibrium distributions of its atoms, e.g., permeation methods, electrochemical methods, and mechanical relaxation methods. The methods of studying random walk may be classified by the method of its observation, e.g., nuclear magnetic resonance (NMR) and quasi-elastic scattering of neutrons.

2.1 Studying hydrogen diffusion under nonequilibrium conditions

Permeability methods of measuring of chemical diffusion coefficient. The simplest experiment of this type involves the passage of hydrogen through a metallic membrane of

thickness s ¹. Suppose that the pressure of molecular hydrogen 'at the inlet' is maintained constant and is equal to p_{in} and the pressure 'at the outlet' is p_{out} . The temperature is assumed to be constant. Then, neglecting surface effects, we can find the density of a stationary flux of hydrogen through the membrane as follows:

$$J = D_{\text{ch}} A(T) s^{-1} \{ \sqrt{p_{\text{in}}} - \sqrt{p_{\text{out}}} \}, \quad (2.5)$$

where $A(T)$ is a temperature-dependent constant that characterizes the shift of the energy reference point upon the passage from the gas phase into the bulk of metal. In this case, hydrogen molecules dissociate at the inlet surface of the membrane and recover at the outlet surface. In reality, one cannot neglect the effect of the kinetics of this process on the rate of hydrogen permeability, which substantially complicates the interpretation of experimental results [16]. In addition, as was noted in the review by Wipf [5, Ch. 7], one should take into account that the processes of absorption and extraction of hydrogen on the sample boundaries should be accompanied by the liberation or absorption of heat. This moment proves to be of fundamental importance in experiments performed under nonstationary conditions, when the hydrogen content in the sample is time-dependent, e.g., when investigating of the kinetics of degassing of hydrogenated samples or, on the contrary, of the hydrogenation of pure metals.

The permeation methods allow one to measure the hydrogen-diffusion coefficient in a wide temperature range up to the melting point [37]. At the same time, we should take into account that, when carrying out experiments by the permeation methods, the hydrogen concentration in a sample may become sufficiently high to provide hydride phases. Therefore, it is necessary to control the experimental conditions in such a way so as to remain in the single-phase region.

This method was used to measure hydrogen diffusion coefficient in the majority of pure metals [11] and alloys and their amorphous modifications [20]. At present, the permeation method is applied rather rarely, since its accuracy is inferior to other methods; therefore, in those cases when there is no need to obtain data in a wide temperature range, other methods are more preferable.

Electrochemical methods. Electrochemical methods are considered in much detail in the review by Züchner [38]. The most perfect of them, which are still applied, are described by Kirchheim and McLellan [39].

The essence of electrochemical methods of measuring diffusion coefficients can be explained in an example of the passage of a single current pulse. Imagine a liquid element consisting of an electrolyte that contains hydrogen ions. Let one of the electrodes be permeable to hydrogen. The electromotive force (emf) of this element depends on the chemical potential and, hence, on the concentration of hydrogen atoms in the electrode. If we apply an external potential difference to this element, a current will flow in the entire cell, whose charge carriers will include hydrogen ions. This will lead to a change in their concentration in the hydrogen-conducting electrode. The rate of relaxation of the emf of the element after the external source is switched off will depend on the rate at which the excess (or deficit) of hydrogen

¹ The description of setups for measuring diffusion coefficients by membrane methods can be found, e.g., in Refs [35, 36].

ions in the electrolyte is compensated by their escape back into the solution. Therefore, the relaxation time is determined by the coefficient of hydrogen diffusion in the electrode. In [39], to realize this method, the authors used a palladium bielectrode in a double cell with a mixture of orthophosphoric acid and glycerol as the electrolyte. The emf of such an element depends on time as follows:

$$\Delta E = \frac{2RTi_0t_0}{F^2c_0(\pi D_{\text{ch}}t)^{1/2}} \exp\left(-\frac{s^2}{4D_{\text{ch}}t}\right), \quad (2.6)$$

where ΔE is the deviation of the emf from the initial value, c_0 is the initial hydrogen concentration in the bielectrode, s is the electrode thickness, R is the universal gas constant, F is the Faraday number, i_0 is the electrical pulse current, and t_0 is the pulse duration.

The electrochemical method of measuring the diffusion coefficient requires careful preparation of the electrode surface in contact with the solution. Indeed, the surface impedance caused by oxidation or contamination of the electrode makes it impossible for hydrogen to escape from the bulk of the electrode into the electrolyte [38]. An important moment is also the need to avoid electrolyte circulation in the cell; it is for this reason that the electrolyte is taken to be as viscous as possible. The use of a liquid as the source of hydrogen ions limits the use of the electrochemical method to a narrow temperature range of 0 to 80°C. The hydrogen concentration in the sample during the experiment, just as in the preceding method, may be relative high; typical values are 10^{-6} to 10^{-1} hydrogen atoms per metal atom [40].

The electrochemical method for determining the hydrogen diffusion coefficient was first applied to palladium and its alloys [38]. At present, it is well suited as the method of determining the permeability of various amorphous alloys and metallic glasses [20] and nanocrystalline materials (see, e.g., [41]).

Gorsky and Snoek effects. The permeation of hydrogen and other interstitial impurities into the bulk of a material is accompanied by the appearance of stresses related to the dilatation of the lattice under the effect of foreign atoms. These stresses can be written [11, Vol. 1, Ch. 3] as

$$\sigma_{ij} = \sum_{\rho=1}^{n_d} P_{ij}^{\rho} c v_{\rho}, \quad (2.7)$$

where P_{ij}^{ρ} is the dipole elastic tensor and v_{ρ} is the occupation of interstices with orientation ρ by hydrogen atoms. In bcc metals three orientations ($n_d = 3$) are possible for octahedral and tetrahedral interstices and the dipole elastic tensor has the form [42]

$$P_{ij}^1 = \begin{pmatrix} A & 0 & 0 \\ 0 & B & 0 \\ 0 & 0 & B \end{pmatrix}, \quad P_{ij}^2 = \begin{pmatrix} B & 0 & 0 \\ 0 & A & 0 \\ 0 & 0 & B \end{pmatrix},$$

$$P_{ij}^3 = \begin{pmatrix} B & 0 & 0 \\ 0 & B & 0 \\ 0 & 0 & A \end{pmatrix}.$$

Therefore, in general, two effects can be observed when an external stress is applied to a sample containing hydrogen atoms: (a) local jumps of hydrogen atoms between orientationally nonequivalent interstices and (b) diffusion at large distances in the presence of a gradient of applied stresses.

The magnitude of the first effect depends on the difference $A - B$; the magnitude of the second effect is determined by the

trace of the dipole elastic tensor $A + 2B$. The first phenomenon is known as the Snoek effect, the second as the Gorsky effect. Both these phenomena can be used to measure diffusion characteristics of hydrogen in metals and alloys.

The observation of the Gorsky effect is carried out as follows [42]. The first way consists in the investigation of elastic aftereffect in a deformed sample. If a constant external load is applied to a spring containing hydrogen as an impurity, the stresses in it will asymptotically tend to a constant magnitude by an exponential law. The time of relaxation of this process is determined by hydrogen diffusion over the bulk of the spring.

The second way is the observation of internal friction peak. Let us consider a rectangular slab of thickness d . When an external periodic load is applied to its surface, the slab begins vibrating with a frequency ω . The hydrogen atoms will move in the sample under the effect of arising stress gradients, producing a resistance to bending due to 'self' stress fields. It was shown in [42] that the movement of hydrogen atoms would be determined by an equation of the following form, which replaces in this case Fick's first law (2.1):

$$\mathbf{J} = -D_{\text{ch}} \nabla \left\{ c - \frac{A + 2B}{3\partial\mu/\partial c} s_{ijkl} \sigma_{kl}(\mathbf{r}, t) \right\}, \quad (2.8)$$

where summation is performed over repeating indices, s_{ijkl} is the tensor of elastic compliances of the material, and $\sigma_{kl}(\mathbf{r}, t)$ is the tensor of external stresses. The Q factor of such an oscillatory circuit is given by the expression [42]

$$Q^{-1} = \Delta_E \frac{96}{\pi^4} \sum_{m=1,3,5} \frac{1}{m^4} \frac{\omega\tau_m}{1 + (\omega\tau_m)^2}, \quad \tau_m = \frac{1}{D_{\text{ch}}} \left(\frac{d}{\pi m} \right)^2, \quad (2.9)$$

where $\Delta_E \sim (A + 2B)^2 / (9\partial\mu/\partial c)$ is the ratio of the inelastic component of deformation (caused by impurity atoms) to the static external deformation. The Gorsky effect permits one to find the magnitude of inelastic stresses related to hydrogen atoms and the coefficient of their chemical diffusion. The latter is calculated from the relaxation time without any additional measurements. The Gorsky effect is used to find hydrogen permeability of metals and alloys at temperatures in a range of 100–500 K and at hydrogen concentrations up to several atomic percent. This method is also suitable for determining diffusion coefficients and their concentration and temperature dependences in amorphous materials (e.g., in the Pd₈₀Si₂₀ alloy [32, Ch. 3]).

The Snoek effect is observed, as a rule, upon the dynamic loading of hydrogenated samples in experiments similar to that described above for the Gorsky effect. The Snoek effect also manifests itself in the form of an internal-friction peak and permits one to determine the time of relaxation of internal stresses, which is related to *local* jumps of hydrogen atoms. For the case of reorientational jumps of a single type, we may write an expression [32, Ch. 3] similar to (2.9):

$$Q^{-1} = A_R \frac{\omega\tau_R}{1 + (\omega\tau_R)^2}, \quad (2.10)$$

where the relaxation time τ_R is, certainly, not related to the coefficient of chemical diffusion. Assuming that the jumps occur via a thermoactivation mechanism, we can write

$$\tau_R = \tau_0 \exp\left(\frac{V}{kT}\right). \quad (2.11)$$

Thus, the Snoek effect permits one to determine the activation energy for hydrogen-atom jumps in the samples studied. The region of applicability of the Snoek effect is the same as that of the Gorsky effect. Note additionally that the methods of mechanical relaxation, in contrast to the previous techniques, are insensitive to the properties of the surface through which hydrogen penetrates into the sample; however, they are very sensitive to crystal-lattice defects. The dynamic Snoek effect can be observed not only upon a mechanical loading of samples; variable internal stresses can be created without external load. As an example, the reorientational magnetic aftereffect due to hydrogen can be mentioned [11, Vol. 1, Ch. 11]. This phenomenon is caused by the interaction of stress fields of domain walls in a ferromagnetic material with a lattice dilatation induced by hydrogen atoms. This effect is observed as a maximum of the amplitude of isothermal relaxation of the specific magnetic resistance $\varrho(T) = [r(t + \Delta t, T) - r(t, T)]/r(t, T)$ (where $r = 1/\chi$ is the magnetic resistance and χ is the initial susceptibility) upon the demagnetization of a sample. For reorientational transitions of a single type, the following relation is valid:

$$\varrho \sim \frac{1 - \exp(-t/\tau_R)}{kT}, \quad (2.12)$$

where τ_R is characterized by Eqn (2.11). The method of magnetic aftereffect has been successfully employed for the determination of the activation energies for hydrogen-atom jumps in nanocrystalline alloys of ferromagnetic metals and for the identification of their chemical surroundings [13].

2.2 Studying hydrogen diffusion under equilibrium conditions

Nuclear magnetic resonance. Nuclear magnetic resonance (NMR) is widely applied for studying diffusion of hydrogen isotopes in various systems, including hydride phases with high hydrogen concentrations, since this method is rather insensitive to the quality of a sample, except for the requirement that it should not contain ferromagnetic impurities. The use of NMR for the determination of parameters of hydrogen diffusion in phases with low hydrogen contents is limited by the sensitivity of the method. There exist two excellent reviews by Cotts [11, Ch. 9; 43] concerning the investigation of hydrogen diffusion by the NMR method; more recent information on this problem can be found in [5, 32]. We will not consider the theory of NMR in our review, since it has been presented in detail in the monograph by Slichter [44]. We confine ourselves to an enumeration of diffusion characteristics of metal–hydrogen systems that can be measured by the NMR method.

The nucleus of a hydrogen atom has an intrinsic angular momentum, i.e., spin \mathbf{s} , and a related magnetic moment $\boldsymbol{\mu} = \gamma \mathbf{s}$ ($\gamma \approx 2.68 \times 10^4 \text{ Hz G}^{-1}$ is the gyromagnetic ratio of a proton). In the presence of a magnetic field $\boldsymbol{\mathfrak{H}}_0 \mathbf{k}$, this magnetic moment precess about the Oz axis with a characteristic Larmor frequency $\omega_0 = \gamma \boldsymbol{\mathfrak{H}}_0$. Relative to an outer observer, a hydrogen atom can be considered as a harmonic oscillator capable of absorbing and radiating energy quanta $\hbar\omega_0$. Such absorption will be observed in a system of protons if an additional weak AC magnetic field $\boldsymbol{\mathfrak{H}}_1 \mathbf{i}$, $\boldsymbol{\mathfrak{H}}_1 \ll \boldsymbol{\mathfrak{H}}_0$ with a frequency ω is applied, e.g., along the Ox axis; at the frequency $\omega = \omega_0$, this absorption will have a delta-like maximum. In reality, the magnetic field at the hydrogen-atom nucleus fluctuates because of interaction with the vibrating metal lattice and fields of other (mobile) hydrogen

atoms. This leads to a broadening of the NMR line. The more intense the proton motion in a sample, the narrower the observed NMR line because of the averaging of fields at the hydrogen-atom nuclei. Measurements of the half-width of the NMR line permits one, thus, to find τ_d — the mean residence time of a hydrogen atom on a lattice site [11, Vol. 1, Ch. 9]. This method is efficient for times corresponding to hydrogen diffusion coefficients in a range of 10^{-15} to $10^{-13} \text{ m}^2 \text{ s}^{-1}$ [5].

The majority of investigations of atomic motion by the NMR method are based on measurements of the time of spin–lattice relaxation T_1 , spin–spin relaxation T_2 , and the time of relaxation of the spin sublattice in the rotating coordinate system $T_{1\rho}$. The time T_1 characterizes the rate of relaxation of the component of the nuclear magnetization parallel to the field $\boldsymbol{\mathfrak{H}}_0$ and T_2 characterizes the relaxation of transverse components of the magnetization. The time $T_{1\rho}$ is especially useful for obtaining information on the low-temperature motion of protons. To measure these quantities, pulse NMR methods are employed [43]. For example, to measure the spin–spin relaxation time, the spin-echo method is used. A sample containing hydrogen atoms is subjected to the action of two specially adjusted pulses of electromagnetic radiation separated by a time interval τ ; in a time equal to 2τ after the first pulse is applied, the NMR spectrometer fixes a signal of a spin echo (pulse of radiation from the sample) whose magnitude is proportional to the modulus of the precessing component of the magnetization perpendicular to the field. The theory gives the following expression for it:

$$\mathfrak{M}_{\text{echo}} = \mathfrak{M}_0 \exp\left(\frac{-2\tau}{T_2}\right), \quad (2.13)$$

where $\mathfrak{M}_0 = \chi_0 \boldsymbol{\mathfrak{H}}_0$ is the stationary value of the z component of the magnetization. From this expression, the time T_2 can be found. With allowance for only magnetic dipole interactions, this time is determined by the expression [44]

$$T_2^{-1} = \frac{3}{32} \gamma^4 \hbar^2 [J^{(0)}(0) + 10J^{(1)}(\omega_0) + J^{(2)}(\omega_0)], \quad (2.14)$$

$$J^{(q)}(\omega) = \int_{-\infty}^{\infty} G^{(q)}(t) \exp(-i\omega t) dt,$$

where $G^{(q)}(t)$ is the two-time correlation function (it is determined by the magnetic dipole–dipole interaction of protons and by the character of their random walk), which cannot be calculated exactly. The simplest approximation suggested by Bloembergen, Purcell, and Pound [*Phys. Rev.* 73 679 (1948)] consists in the assumption that the decay of the correlation of dipole fields is described by an exponential law $\exp(-t/\tau_c)$ with a single correlation time τ_c . Then, we have

$$J^{(q)}(\omega) = G^{(q)}(0) \frac{2\tau_c}{1 + (\omega\tau_c)^2}. \quad (2.15)$$

For pairwise hydrogen–hydrogen interactions, this time is usually assumed to be $\tau_c = \tau_d/2$. Note that Eqn (2.14) is valid only for relatively small relaxation times, when $T_2^{-1}\tau_c \ll 1$. The range of the residence times measured by pulse methods corresponds to hydrogen-diffusion coefficients of 10^{-17} to $10^{-10} \text{ m}^2 \text{ s}^{-1}$ [32, Ch. 3].

The phenomenon of nuclear magnetic resonance permits one, apart from determining the mean residence time, to *independently* find the coefficient of hydrogen diffusion in a metal. Suppose that there exists a permanent gradient of the

magnetic-field strength along the Oz axis: $\mathfrak{G} = \partial\mathfrak{H}_z/\partial z$. Then, during random walk of a proton the Larmor precession frequency will fluctuate, which will lead to an additional broadening of the NMR line. It can also be shown [44] that the presence of a field gradient leads to an increase in the rate of the decrease in the intensity of the spin-echo signal. For the simplest two-pulse spin-echo scheme, Eqn (2.13) is modified to the form

$$\mathfrak{M}_{\text{echo}} = \mathfrak{M}_0 \exp \left\{ -\frac{2\tau}{T_2} - \frac{2}{3} (\gamma\mathfrak{G})^2 D_{\text{rw}}\tau^3 \right\}. \quad (2.16)$$

It is, therefore, clear that the two-pulse method of measuring spin echo permits one to simultaneously determine the time of spin–spin relaxation (and, consequently, the correlation time) and the hydrogen diffusion coefficient. More perfect multiple-pulse techniques of measuring spin echo exist [11, Vol. 1, Ch. 9], which have the advantage that their results are independent of the magnetic-field inhomogeneities that are always present in samples. According to [32, Ch. 3], the method of magnetic-field gradient permits one to measure the hydrogen diffusion coefficient in a range of 10^{-12} to $10^{-18} \text{ m}^2 \text{ s}^{-1}$. The independent knowledge of the diffusion coefficient and the residence time of impurity atoms permits one to find the average square of the diffusion step using Eqn (2.2), where the role of $\sqrt{\langle R^2 \rangle}$ is played by the length of the diffusion step and where the mean residence time τ_d substitutes for the time t .

The NMR method is mainly employed to study crystalline metals and alloys; few works are known where this technique is applied to amorphous alloys [32] and nanocrystalline alloys [45, 46].

Quasi-elastic neutron scattering. Among the methods that permit one to study metal–hydrogen systems on a microscopic level, special place belongs to the quasi-elastic neutron scattering (QNS) method for several reasons. First, neutrons only weakly interact with matter and can easily penetrate into a material, which permits them to be efficiently used for studying mass transport in the bulk of a material. Second, the wavelength of thermal neutrons is comparable to interatomic distances and their energy is on the order of that characteristic of typical phonon excitations of crystal lattices. Finally, neutron scattering by protons is spin-dependent. However, proton spins are disordered in direction in the material because of thermal fluctuations; therefore, the scattered waves will not interfere and neutron scattering in this case will be incoherent. This means that neutron scattering by protons gives information on the individual motions of hydrogen atoms in the sample, whereas for deuterium and tritium, on the contrary, data on their collective behavior will be obtained.

When conducting neutron experiments, the quantity to be measured is the double differential scattering cross section $\partial^2\sigma/(\partial\Omega\partial\omega)$ (per unit solid angle Ω and unit angular frequency interval ω) [47], which is proportional, to an accuracy of a known factor, to the structure factor

$$S_{\text{inc}}(\mathbf{q}, \omega) = \frac{1}{2\pi} \iint G(\mathbf{r}, t) \exp [i(\mathbf{q} \cdot \mathbf{r} - \omega t)] \mathbf{dr} dt, \quad (2.17)$$

where \mathbf{q} is the difference of the wave vectors of the scattered and incident neutrons, $\hbar\omega$ is the energy transferred in the scattering event, and $G(\mathbf{r}, t)$ is the autocorrelation function. In the classical approximation, the magnitude of $G(\mathbf{r}, t)$ yields the probability that the proton located at $t = 0$ at the origin

will have a position vector \mathbf{r} at the time moment t . The $G(\mathbf{r}, t)$ function may be calculated in terms of a simple but, nevertheless, constructive Chudley–Elliott’s model [*Proc. Phys. Soc.* **77** 353 (1960)]. The principal points of this model are as follows:

- (a) a diffusing particle moves from one position to another nearest position by a random instantaneous jump;
- (b) the positions available for hydrogen atoms form a simple Bravais lattice;
- (c) diffusional jumps do not correlate with thermal vibrations of a proton in the equilibrium position; and
- (d) the interaction between hydrogen atoms is negligible and exerts no effect on their motions.

Then, with allowance for the fact that in the QNS method, neutrons with small scattering vectors are detected ($qa \ll 1$, where a is the lattice parameter), the incoherent structure factor can be written in the form [11, Vol. 1, Ch. 10]

$$S_{\text{inc}}(q, \omega) = \frac{1}{\pi} \exp [-q^2 \langle u^2 \rangle] \frac{D_{\text{rw}} q^2}{\omega^2 + (D_{\text{rw}} q^2)^2}, \quad (2.18)$$

where the exponent represents the conventional Debye–Waller factor with a mean squared amplitude of thermal vibrations of a proton in the equilibrium position $\langle u^2 \rangle$.

The QNS method makes it possible to determine the diffusion coefficient in hydride phases at hydrogen concentrations greater than 0.1 at.% [32, Ch. 3]. This method is suitable for both crystalline materials and amorphous alloys. The sensitivity of the method is limited by the resolution of neutron spectrometers. The forward-scattering spectrometers are efficient in studying processes with relaxation times τ_d no more than 10^{-11} s [11, Vol. 1, Ch. 9]; the high-resolution backscattering spectrometers extend this limit by two orders of magnitude.

3. Theoretical concepts

The ways of describing atomic diffusion in disordered media are distinguished in both the type of formalism underlying the calculation of the diffusion coefficient and in the method of simulation of the disordered medium. Although the models of disorder are quite varied, they can be conditionally divided into two groups according to the way the diffusion coefficients are determined. This division in fact corresponds to the previously accepted classification of the experimental methods of determination of the diffusion coefficient into equilibrium and nonequilibrium ones.

The first approach is based on the consideration of random walk of a tracer and the asymptotic relationship between the mean square of its displacement and the time of motion (2.2). The second approach implies the existence of a driving force resulting in a macroscopic flow of diffusing atoms. The gradient of chemical potential (in the simplified situation, the gradient of concentration) of the impurity atoms can play the role of such a force. Then, based on the model of a disordered medium, we obtain a relationship between the flux of atoms and the gradient of their concentration in the form of Fick’s first law (2.1) or an expression in the form of Fick’s second law:

$$\frac{\partial c}{\partial t} = D_{\text{ch}} \Delta c, \quad (3.1)$$

in which the coefficient of proportionality D_{ch} is the coefficient of chemical diffusion. The problem of establish-

ing a general relation between the coefficients D_{rw} and D_{ch} for arbitrary disordered media has been discussed in [48] but is far from being solved.

3.1 Random-walk method

The works in this direction are mainly devoted to systems with a crystal disorder. They can be divided into two groups.

In Refs [49–52], it is assumed that crystal disorder can be taken into account by introducing distributions of potential energies of diffusing atoms in sites of a regular crystal lattice (residence sites of hydrogen in a metal) and in saddle positions. (These distributions were assumed to be mutually independent.)

In Refs [49, 50], random walks of an ensemble of noninteracting particles on a cubic lattice of arbitrary dimensionality d were considered. In the case of $d = 1$, an exact expression for the Einstein diffusion coefficient was found:

$$D_{rw} = D_0 \frac{\langle \exp(\beta \varepsilon_{ij}) \rangle^{-1}}{\langle \exp(-\beta \varepsilon_i) \rangle}, \quad (3.2)$$

where D_0 is the prefactor (the determination of its value is beyond the scope of the theory), $\beta = 1/(kT)$, angular brackets (...) mean averaging over the ensemble of systems, ε_i is the energy of an impurity atom on site i , and ε_{ij} is the potential barrier between a pair of sites (energy in the saddle point of the $i \rightarrow j$ transition). At $d > 1$, the effective-medium approximation was introduced, from which it follows that Eqn (3.2) is valid also at $d \rightarrow \infty$. At $d = 2$ and 3, more complex dependences of the diffusion coefficient on the energy distributions are obtained, which can be concretized only for a limited class of problems. In Ref. [50], the authors performed a calculation for $d = 3$ and 5 for the case of uniform distribution of sites and saddle-points in energy (the probability of finding a site or a saddle point with an energy ε is independent of ε) and Gaussian energy distributions:

$$n(\varepsilon) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left\{-\frac{\varepsilon - \bar{\varepsilon}}{2\sigma^2}\right\}, \quad (3.3)$$

where $\sigma = \sigma_c$ and $\bar{\varepsilon} = \bar{\varepsilon}_c$ for the saddle points, and $\sigma = \sigma_s$ and $\bar{\varepsilon} = \bar{\varepsilon}_s$ for the sites. In addition, a comparison of the results of the effective-medium approximation with the results of numerical experiments was performed. It was shown that in both cases the effective-medium approximation works well for weak disorder with the temperature dependence of the diffusion coefficient only weakly deviating from the Arrhenius law. The latter becomes clear from the results of Ref. [52], where the random walk of particles is considered in a somewhat different way, although the same assumptions as in Refs [49, 50] are used. The diffusion coefficient at small concentrations of an impurity and low temperatures (when only the fastest diffusion paths are efficient) is written as

$$D_{rw} = D_0 \exp\left\{-\beta(\varepsilon_c - \varepsilon_s) + \frac{\beta^2}{2}(f\sigma_c^2 - \sigma_s^2)\right\}, \quad (3.4)$$

where f is a smoothly varying function of $\beta\sigma_c$, which depends on the crystal-lattice type. As is seen from Eqn (3.4), the contributions from the disorder in the energies of the saddle points and the residence sites of the diffusant atoms to the non-Arrhenius term compensate each other. This is apparently a consequence of the adopted hypothesis of the

independence of the energies of atoms located in the saddle points and interstices.

In this connection, of significant interest is Ref. [53], in which an analogy between the diffusive and electrical conductivities of disordered media [54] is used. The authors of [53] consider random walk of hydrogen atoms in a two-component system consisting of regularly arranged cubic crystallites embedded into a matrix, which can be both crystalline and energetically disordered with Gaussian distributions of the energies of protons located in interstices and in saddle points, similar to Eqn (3.3). The material is characterized by the diffusion coefficients D_M in the matrix and D_G in grains and by the quantities D_{MG} and D_{GM} that determine the exchange of atoms between the subsystems. These coefficients are proportional to the average frequencies of hydrogen-atom jumps

$$\begin{aligned} D_G &\sim \frac{1}{\tau} \exp(-\beta V_G), \\ D_M &\sim \frac{1}{\tau} \frac{(1 - c_M)^2}{c_M} \exp(\beta \mu_M) \langle \exp(-\beta V_M) \rangle, \\ D_{GM} &\sim \frac{1}{\tau} (1 - c_M) \langle \exp(-\beta V_{GM}) \rangle, \\ D_{MG} &\sim \frac{1}{\tau} \frac{(1 - c_M)(1 - c_G)}{c_M} \exp(\beta \mu_M) \langle \exp(-\beta V_{MG}) \rangle, \end{aligned} \quad (3.5)$$

where the quantities with the indices G and M refer to the crystallites and matrix, respectively, and μ , c , and V are the chemical potential, concentration of hydrogen atoms, and the energy of activation for a diffusion jump, respectively (expressions (3.5) have been written following Ref. [18]). The equilibrium concentrations and chemical potentials c_i and μ_i ($i = M, G$) can be found using computer simulation or methods of statistical physics. It follows from the solution of the simplified problem that there is an analogy between the electrical conductivity and the product $c_i D_i$ ($i = M, G$). Based on this analogy, approximate ‘network’ models were constructed in [53], which represented various combinations of ‘matrix’ and ‘crystallite’ conductors connected in series and/or in parallel, suitable for finding the effective diffusion coefficient of hydrogen in the disordered medium considered. A comparison of the results of calculations using these models with Monte Carlo calculations showed good applicability of the models at arbitrary concentrations of hydrogen atoms in a wide range of theory parameters. According to the authors of Ref. [53], the models suggested can be applied to virtually any statistically isotropic two-component systems, since the results of computer calculations proved to be only weakly sensitive to the shape, size, and spatial distributions of crystallites in the matrix.

In other works, based on the theories of fractals and percolation (see, e.g., review [55]), the geometrical nature of disorder was taken into account in the explicit form. Note that these models of disordered systems have an artificial character (e.g., frequently, random walk of a particle on a Sierpinsky carpet or Sierpinsky sponge is considered); therefore, it is quite difficult to compare them with real systems.

One of the most important results of this activity is the proof that diffusion in spatially disordered structures may have an anomalous character (see, e.g., a detailed review in Ref. [34]); i.e., instead of Eq (2.2), the following dependence is fulfilled:

$$\langle R^2(t) \rangle \sim t^{2/d_t}, \quad (3.6)$$

where $d_f > 2$ is a characteristic of the material (its fractal dimension). The quantity d_f in the percolation theory is related to critical exponents. The principal point is the assumption that in a disordered lattice there exist random positions occupied by diffusing atoms that form a cluster. The percolation model was exactly solved for a square lattice. If the fraction of randomly occupied positions is p and if p increases, then there exists a critical value $p_c = 0.592745$ such that at $p > p_c$ an infinite cluster is formed in the system (i.e., applying to a particular situation, mass transfer is realized over positions with a small activation energy). The fractal dimension of such a cluster is

$$d_f = d - \frac{\beta_0}{\nu}, \quad (3.7)$$

where β_0 and ν are critical exponents of the percolation theory, which for a planar lattice are $\beta_0 = 5/36$ and $\nu = 4/3$. For a three-dimensional disordered material, d_f can be found only by numerical simulation [55].

Computer investigation of random walk of particles in disordered media shows that its results agree with the results of analytical calculations. It follows from a series of works [56–58] on computer simulation that the effective energy of activation for Einstein diffusion of hydrogen on a disordered lattice depends on temperature and decreases with an increase in hydrogen concentration. A deviation of the temperature behavior of the average time between hydrogen-atom jumps from the Arrhenius law increases with increasing impurity content. It was shown that a comparison of the calculated and experimental curves of quasi-elastic neutron scattering by hydrogen atoms makes it possible to estimate the degree of disorder in the amorphous alloy.

Note that the analytical investigation of the concentration dependence of Einstein diffusion coefficient is very difficult in view of the complexity of taking this dependence into account in terms of the random-walk method. This explains why works of this type are so rare in publications devoted to the investigation of hydrogen diffusion in disordered materials.

3.2 Trap model

One of the first theoretical works on the diffusion of hydrogen in a disordered system was the paper by McNabb and Foster [59] devoted to the explanation of the deviation from Fick's law (2.1) for hydrogen diffusion in steels at temperatures below 400 °C. The authors assumed that the hydrogen atoms may be located both in normal positions and on traps, which possess a property to capture an impurity atom. The traps themselves have a statistically uniform distribution in the material and their only characteristic is concentration N . Then, one can easily include a term related to the impurity atoms located on traps into the equation for Fick's second law and supplement it with a second balance equation — for immobile hydrogen atoms. As a result, the following set of two differential equations is obtained:

$$\frac{\partial C}{\partial t} + N \frac{\partial n}{\partial t} = D\Delta C, \quad (3.8)$$

$$\frac{\partial n}{\partial t} = kC(1 - n) - pn,$$

where C is the concentration of mobile hydrogen, n is the fraction of occupied traps, and k and p are the parameters of

the theory. Analysis shows that the effective (experimentally observed) hydrogen diffusion coefficient in a massive sample is $D/(1 + Nk/p)$. In addition, many anomalies of diffusional behavior of hydrogen in steels were described qualitatively. A disadvantage of the approach is the allowance for only one type of trap and the impossibility of determining the diffusion coefficient in view of the presence of free parameters in the theory.

The first of these disadvantages was completely eliminated in the work by Leblond and Dubois [60]. The authors supposed that all hydrogen-atom positions can be divided into a finite number of classes. The positions of the first type are usual sites; the positions of other types are traps. There was introduced a probability $g_{kl}(\mathbf{r}, \mathbf{r}', t) d\mathbf{r}' dt$ that the atom located at a time moment t in an interstice of type k at point \mathbf{r} passes after a time dt into a position of kind l located in the vicinity $d\mathbf{r}'$ of the point \mathbf{r}' . Then, using this function, a statistical transport equation of the Boltzmann type was constructed and relationships for the partial concentrations of impurity on positions of various types were found using a number of plausible approximations concerning the type of the function. These relationships had the form of the generalized Fick's second law and included, along with the diffusion terms of the type (3.1), terms that describe the local exchange between positions leading to the establishment of a thermodynamic equilibrium [these corrections are similar to the right-hand side of the second equation of set (3.8)]. It was also shown how, after the specification of the types of traps, these results could be reduced to the results of other, simpler models (including the McNabb–Foster theory). Note that the Leblond–Dubois approach, like that of the above authors, makes it possible to study nonstationary regimes of diffusion. At the same time, a large number of phenomenological parameters describing traps were introduced into the theory, so that its comparison with experiment turned out to be difficult. The blocking effects have not been taken into account either. In addition, the Leblond–Dubois approach does not make it possible to analyze the concentration dependence of the effective diffusion coefficient.

Now, we proceed with a review of microscopic models, which substantially restrict the number of free parameters of the theory. In this connection, of large interest is the work by Kirchheim [27] concerning materials with a single type of trap, similar to those that have been studied by McNabb and Foster, and the generalization of this approach to a more complex case of binary alloys with a bcc lattice in the work by Brower et al. [61].

It is assumed in the Kirchheim model applied to dilute binary alloys that

(a) the interstices over which impurity atoms move can be divided into two classes: normal positions and traps, i.e., interstices in which the proton energy is lower by $-\varepsilon_t$ than in normal positions. The appearance of traps (in the general case these can be obstacles with $-\varepsilon_t < 0$) is associated with the presence of atoms of an alloying element in the metal;

(b) no correlations in the location of traps exist;

(c) the energies at the saddle points between positions of various types are equal;

(d) there exists a local equilibrium at which the population of interstices (pores) with hydrogen atoms is described by the Fermi–Dirac distribution

$$v_i = \frac{1}{1 + \exp\{\beta(\varepsilon_i - \mu)\}}, \quad (3.9)$$

where $i = 1, 2$ denote the types of interstices (normal pore, trap), and ε_i is the proton energy in an interstice of type i ; and

(e) the probability of the transition $i \rightarrow j$ is proportional to the frequency factor of type (1.1) [where the activation energy is equal to the difference between the energy at the saddle point and ε_i] and to the product $v_i(1 - v_j)$.

Then, in the lowest approximation in hydrogen concentration, the following expression is obtained for the diffusion coefficient:

$$D_{\text{ch}} = \frac{D_0}{1 - C_t^0 + C_t^0 \exp(-\beta\varepsilon_t)}, \quad (3.10)$$

where D_0 is the coefficient of diffusion in pure metal and C_t^0 is the concentration (fraction) of traps.

3.3 Method of configuration sums

The work by Brower et al. [61] substantially refines the Kirchheim model, since

(a) it assumes that the interstices are divided into five types according to the numbers of atoms of unlike kind in the nearest neighborhood of an interstice;

(b) it takes into account the circumstance that the interstices completely surrounded by different atoms of different types cannot be nearest neighbors;

(c) it accounts for the hydrogen–hydrogen interaction, which is described by the term $f(c)$ in the Fermi–Dirac distributions law

$$v_i = \frac{1}{1 + \exp\{\beta(\varepsilon_i + f(c) - \mu)\}}; \quad (3.11)$$

(d) it takes into account the effect of blocking of neighboring interstices by hydrogen atoms.

In this case, the hydrogen diffusion coefficient after averaging over all possible types of $i \rightarrow j$ transitions has the form

$$D_{\text{ch}} = \sum_{i,j} D_{ij}^0 \beta M B_{ij} v_i [1 - v_j s_j] \exp\{-\beta V_{ij}(c)\} \frac{\partial \mu}{\partial c}, \quad (3.12)$$

where the quantity D_{ij}^0 (equal to the product of the length of an $i \rightarrow j$ jump by the frequency of attempts to realize such a jump) is linearly interpolated between the experimentally known values for an $i \rightarrow j$ jump in pure metals; M is the number of interstices per unit volume of the alloy; B_{ij} is the probability of finding a pair of neighboring interstices of types i, j ; s_j is the coefficient of blocking of interstices, which is determined from the assumption that a hydrogen atom located in a pore j blocks all nearest empty interstices of the same type; and $V_{ij}(c)$ is the energy of activation for an $i \rightarrow j$ jump, which (like the energy of a hydrogen atom in the equilibrium position ε_i) is determined from experimental data or computer simulation. To calculate chemical potential, one should know the energy $f(c)$, but its determination lies beyond the scope of the theory.

The application of the Brower theory to Nb–V alloys showed satisfactory agreement with experiment. At the same time, this theory also contains a large number of parameters and requires additional data to determine them. In addition, both the Kirchheim approach [27] and the Brower theory [61] have a common shortcoming: the populations of the pores v_i and v_j , which are the initial and final positions of a hydrogen

atom upon a diffusion event, are calculated at the same magnitude of the chemical potential. In reality, the values of the chemical potential for these states are different because of the presence of a macroscopic gradient of concentration of hydrogen atoms. At a large hydrogen concentration, this can lead to an incorrect magnitude of the diffusion coefficient.

The Brower approach was refined by Biscarini et al. [62], who additionally took into account orientationally nonequivalent configurations of interstices in binary alloys. An important point is also the assumption of the possibility for hydrogen atoms to occupy pores of different types, e.g., tetrahedral and octahedral interstices in bcc alloys. The authors of Ref. [62] systematically derived analytical expressions for the blocking factors, distributions function (3.11), and thermodynamic potentials of hydrogen atoms with allowance for their mutual repulsion at small distances.

Note that the idea of summation over all possible configurations of matrix atoms surrounding a proton, which was used by Brower, was first suggested by Krivoglaz and Smirnov [63] in connection with the problem of finding the diffusion coefficient of an interstitial impurity in ordering alloys. Later, their theory was applied to hydrogen diffusion in alloys of the Cu₃Au type [64]. Vykhodets et al. [64] assumed that diffusion of protons in an ordering alloy with a β -brass structure occurs via jumps along a chain of interstices of the octahedral–tetrahedral–octahedral type. They assumed that the hydrogen concentration is small and, therefore, there was no need to take into account the interaction of hydrogen atoms with each other or the blocking effects. Then, Eqn (3.9) turns into a Boltzmann distribution. Further, summation over all possible types of transitions and all interstice configurations was performed. The interstice configurations were determined by the arrangement of metal atoms around a hydrogen atom up to the fourth coordination shell. When calculating proton energies in the lattice, their interaction with matrix atoms in four coordination shells was taken into account; the energy in saddle points was determined by the arrangement of metal atoms in nine coordination shells. The probabilities of occupation of lattice sites by metal atoms of various types, which determined the interstice configurations, were calculated using the theory of regular solid solutions. In the end, the hydrogen diffusion coefficient was expressed through the degree of order in the alloy and 34 (!) parameters characterizing metal–hydrogen interaction. They can be calculated given a concrete form of the potential of interaction is specified (the authors of [64] used the Morse potential). The model suggested in [64] correctly describes the behavior of the diffusion coefficient upon the order–disorder transition. Good quantitative agreement is observed only for the Ni₃Fe alloy, which apparently better satisfies the assumptions adopted in calculations of the energy of metal–hydrogen interaction.

It follows from the above examples that the key problem, when finding the hydrogen diffusion coefficient in alloys with chemical disorder, remains the problem of determining the characteristics of the potential relief of a proton in the alloy and the problem of their relation to the observed quantities. The same problem takes place in the theory of diffusion in crystalline disordered systems.

3.4 Systems with crystalline disorder

The most common and virtually the only approach that makes it possible to calculate the chemical diffusion coefficient of hydrogen in amorphous metals is the Kirchheim

model [27], which represents a generalization of the approach, previously developed by the same author for finding the hydrogen-diffusion coefficient in dilute binary alloys, to the case of a continuous distribution of the energies of hydrogen atoms located in (quasi) interstices. This distribution is usually approximated by a Gaussian curve (3.3). Then, the effective diffusion coefficient is written as²

$$D_{\text{ch}} = D_{\text{hyp}} \sqrt{2\pi} \sigma \beta \exp \left\{ \left[\text{erf}^{-1} |2C - 1| \right]^2 - \sqrt{2} \beta \sigma \text{erf}^{-1} |2C - 1| \right\}. \quad (3.13)$$

Here, D_{hyp} is the hydrogen diffusion coefficient in a 'hypothetical' metal that is characterized by the average energy $\bar{\epsilon}$; $C = c/M$ is the dimensionless concentration of hydrogen atoms; and erf^{-1} is the inverse of the error function ($x = \text{erf}^{-1} \gamma$ is equivalent to $\gamma = 2/\sqrt{\pi} \int_0^x \exp(-x^2) dx$). This expression was obtained under two conditions: first, it was assumed that the hydrogen concentration is small as compared to unity; and, second, the Fermi–Dirac distribution (3.9) was taken in the form of a step. The second condition restricts the applicability of Eqn (3.13) from below by the magnitude of the impurity concentration. In Ref. [27], Kirchheim compared the calculated concentration dependence of the hydrogen diffusion coefficient in the amorphous alloy $\text{Pd}_{77.5}\text{Cu}_6\text{Si}_{16.5}$ at hydrogen contents of 10^{-5} to 10^{-1} atoms per metal atom at room temperature with experimental data. The magnitude of σ was taken from the data of an additional experiment designed to determine the concentration dependence of the chemical potential of protons in an amorphous material. The coefficient D_{hyp} played the role of an adjusting parameter. According to the author of [27], the agreement of the theory and experiment was satisfactory. In our opinion, however, it is difficult to say, taking into account the above remarks and the utilization of the procedure of fitting, whether this agreement was a fundamental confirmation of the validity of the approach employed or a consequence of fitting.

The problem of the relation of the parameters of the hydrogen-atom-position distribution (3.3) with the data of other, nondiffusional, experiments was discussed by Kirchheim et al. in Ref. [40]. The authors argued that the half-width of this distribution should be proportional to the half-width of the first peak of the radial distribution function of atoms in an amorphous material. In more detail, the problem of a potential relief of protons in amorphous metals was considered by Richards [65], who showed that the half-width of the distribution of hydrogen atom energies in the interstices of an amorphous metal can be written as

$$\sigma = 3KV_{\text{H}}N^{-1/2}\sigma_1, \quad (3.14)$$

where K is the bulk modulus of the metal, V_{H} is the partial molar volume of hydrogen, N is the number of edges of a polyhedron representing the shape of the quasi-interstice occupied by a hydrogen atom, and σ_1 is the half-width of the first peak of the radial distribution function of metal atoms (it is assumed that this function is also approximated by a Gaussian). At the same time, Richards [65] indicated the need to take into account the saddle-point energy distribution when finding the effective activation energy. However,

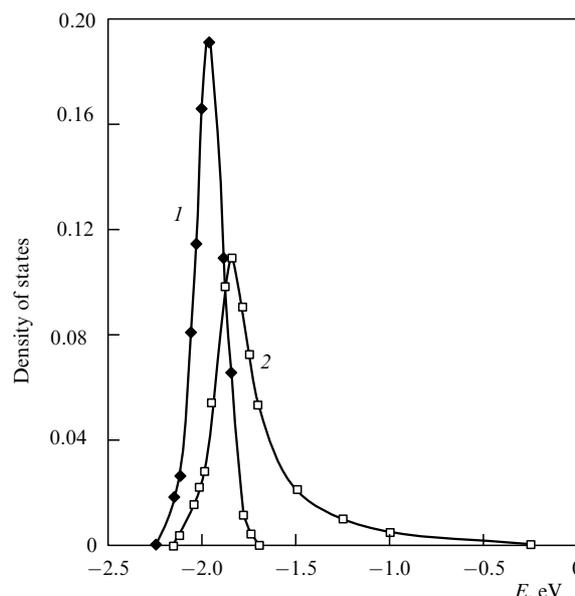


Figure 3. Distribution of the energies of hydrogen atoms in amorphous iron according to the data of computer simulation [66]: (1) equilibrium positions (quasi-interstices) and (2) saddle points.

no simple expression similar to Eqn (3.14) can be written for this energy, since the lattice deformation upon the passage of a hydrogen atom through a saddle point cannot be measured experimentally. Instead, one must resort to model considerations concerning the form of the metal–hydrogen interaction potential. In the review by Belashchenko [66], data of computer simulation of hydrogen diffusion in iron are given (see Fig. 3). These data confirm the fact indicated by Richards: in an amorphous metal, a continuous distribution of hydrogen-atom energies does take place both in equilibrium positions and in saddle points, and the half-width of the latter is twice as large as that of the former. Hence, a significant drawback of the Kirchheim theory is neglecting the energy distribution in saddle points.

Another important disadvantage of the Kirchheim approach is the assumption of the presence of a single continuous distribution of the position energies of hydrogen atoms in alloys. A comparison of the data on hydrogen diffusion in amorphous Pd–Si and Ni–Zr alloys obtained by nonequilibrium and equilibrium methods, as well as of the data of computer simulation [32, Ch. 3], permitted one to draw an important conclusion. The data of electrochemical analysis and the Gorsky effect can be satisfactorily explained by the presence of a single continuous energy distribution whereas the results of NMR and QNS studies can be explained on the assumption that in amorphous systems several clearly separated energy bands exist, leading to substantially different time dependences of mass transport. The assumptions necessary to correctly describe the solubility of hydrogen in amorphous alloys of transition metals [67] and the direct measurements [24] showed that the spectrum of hydrogen-atom energies in amorphous alloys represents a sum of clearly resolved bell-shaped curves centered at the positions corresponding to a definite surrounding of protons with metal atoms of different types. For Ni–Zr alloys, these are tetrahedral configurations such as Zr_4 , NiZr_3 , and Ni_2Zr_2 (see Fig. 2). Another example is the computer simulation of the amorphous iron–hydrogen system [68]. It was shown in

² In Ref. [27], expression (3.13) was written with a plus sign in front of the last term in the exponent, which is a result of a misprint in the paper. This formula with a wrong sign is, however, frequently cited in the literature.

this work that in amorphous iron, protons occupy positions that can clearly be subdivided into two types: deep potential wells with a hydrogen coordination consisting of 6–9 metal atoms (these are mostly distorted octahedra) and high-energy positions with a coordination number of 4–6. Note that the largest pores are not energetically favorable for the location of hydrogen atoms in them. The difference in the data obtained by equilibrium and nonequilibrium methods is explained by the fact that at small deviations from equilibrium in narrow temperature ranges (which are characteristic, e.g., of electrochemical methods) a significant contribution to mass transport comes from a relatively small group of atoms with nearly equilibrium values of the chemical potential of hydrogen at its given concentration, corresponding to a narrow part of the energy spectrum. The methods that are sensitive to relaxation processes in a wide time interval, e.g., NMR, on the contrary, ‘illuminate’ the entire distribution of hydrogen-atom energies in equilibrium positions.

Now, we pass to nanocrystalline metal–hydrogen systems. The majority of reviews on diffusion in these systems [21–23] from the end of the 1980s up to now concern the results of Kirchheim’s work [18], who extended the theory of diffusion in amorphous systems [27] to the case of metals in the nanocrystalline state. It was supposed that this state represented a mixture of two structural components: an intergrain amorphous-like component (boundary) and a crystalline component. Correspondingly, the calculation of the diffusion coefficient using the Kirchheim method was carried out with the energy distribution in the form of a sum of a Gaussian curve and a delta-like peak corresponding to crystallites. For nanocrystalline palladium, a comparison of the theory with experiment [26] was performed, which showed a qualitative agreement: the diffusion coefficient in nanocrystalline samples first was smaller than in polycrystals but rapidly grew with increasing hydrogen concentration and exceeded its value for polycrystalline samples. However, as was shown experimentally, its growth was substantially limited by the mutual repulsion of hydrogen atoms. This is confirmed by Fig. 1 borrowed from Ref. [26]. The calculated dependence of the diffusion coefficient of hydrogen on its concentration in nanocrystalline palladium without allowance for proton repulsion is shown in this figure by a dashed line, and that with allowance for repulsion by a solid line.

Since the allowance for hydrogen interaction has not been built into the Kirchheim approach [27], it is impossible to write a more exact analytical expression for the diffusion coefficient in this case. A computer calculation of the diffusion coefficient with allowance for proton repulsion made it possible to determine the parameters of the potential relief of hydrogen atoms in grain boundaries of nanocrystalline palladium, i.e., the average energy and the half-width of the energy distribution in quasi-interstices. It is clear that the model developed in Ref. [18] describes, in fact, the quasivolume diffusion, when hydrogen transport is realized through both grain boundaries and the bulk of grains but because of the high permeability of the boundaries the main flow of the diffusant occurs in the intergranular space. Meanwhile, Marte and Kirchheim [31] observed, in their work devoted to hydrogen diffusion in nanocrystalline nickel, a transition from grain-boundary to purely bulk regime of hydrogen diffusion upon an increase in the temperature of preliminary annealing of the samples. The authors of [31] ascribe this to structural relaxation in grain boundaries rather than to a change in the fraction of various components of the material.

It is understandable that the entire variety of diffusion regimes in this case cannot in principle be described in terms of the Kirchheim approach, which implies the existence of local equilibrium in the bulk of the material, i.e., rigidly fixes the relationship between the concentrations of hydrogen in grain boundaries and in the bulk of grains. Thus, it is indicated in the paper by Divinskii and Larikov [54] that diffusion in multiphase systems is determined not only by the volume fractions of individual components but also by their mutual geometrical arrangement. This arrangement plays an especially important role when the fractions of the components of the material are comparable. It is precisely this situation that is realized in metals in the nanocrystalline state. At present, no consistent microscopic theory of hydrogen diffusion that takes into account these circumstances exists.

When analyzing this problem, one should pay attention to the phenomenological theory of Aifantis [69] concerning diffusion in a medium containing n different families of diffusion paths. Each path is continuously distributed over the volume of the sample and is characterized by its diffusion coefficient. It is supposed that there exists mass exchange between these paths, which is described by linear equations. As a result, a set of coupled differential equations of reactive diffusion can be written. The mathematical analysis was performed for the case of $n = 2$, when the equations have the following form [cf. with the McNabb–Foster problem (3.8)]:

$$\begin{aligned}\frac{\partial c_1}{\partial t} &= D_1 \Delta c_1 - k_1 c_1 + k_2 c_2, \\ \frac{\partial c_2}{\partial t} &= D_2 \Delta c_2 - k_2 c_2 + k_1 c_1,\end{aligned}\tag{3.15}$$

where $D_{1,2}$ are partial diffusion coefficients, $c_{1,2}$ are the concentrations, and $k_{1,2}$ are the coefficients of exchange between the paths. The simplest solution to this set of equations was obtained for a semi-infinite medium (see Refs in [70]). The recent analysis of Aifantis et al. [70, 71] confirmed the physical applicability of this model. It proved to be suitable for description of both diffusion in single crystals with a high density of dislocations (Ca^{2+} in MgO and self-diffusion in gold) and grain-boundary diffusion (Co_{60} in polycrystalline γ -Fe, self-diffusion in copper). In the latter case, the role of different diffusion paths is played by grain boundaries and the bulk of grains. It is noted [71] that in terms of this approach the coefficients $k_{1,2}$ have the sense of microscopic parameters that describe the exchange of atoms between the grain and the boundary.

Turning back to the problem of hydrogen diffusion in nanocrystalline materials, we note that a perspective and important problem of the theory is building a bridge between the microscopic approaches like that of Kirchheim [18, 27] and the phenomenological models such as those due to Aifantis [69] and McNabb and Foster [59]. This would permit us to substantially advance in the understanding of the processes of mass transport in disordered media.

In Refs [72–74] a general approach based on the method of configuration sums is suggested, which makes it possible to write the expression for the coefficient of chemical diffusion of hydrogen in disordered alloys in a sufficiently simple way. The advantage of this approach is that it permits one to easily extend the theory to the case of amorphous and partially crystalline systems [75–77]. The theory developed in the

above works makes it possible to determine the temperature and concentration dependences of the coefficient of chemical diffusion of hydrogen in amorphous metals and alloys and relate the parameters of the theory to the characteristics of their microstructure determined from independent experiments.

4. Development of the theory of hydrogen diffusion in disordered alloys (method of configuration sums)

General formalism [75]. The microscopic theory of diffusion [78] considers the displacement of a given interstitial atom in a force field produced by its surroundings. It is assumed that the noninteracting hydrogen atoms in a disordered material move through a stationary potential relief. The potential minima correspond to (quasi) interstices, or pores. In each pore only one proton can reside. The probability of an atom jumping from one interstice into another is described by Eqn (1.1), where V is the minimum kinetic energy that a hydrogen atom obtains from its neighbors as a result of a fluctuation.

Let there be a gradient of impurity along the x axis. Then, according to the hypothesis of local equilibrium [79], the entire space can be divided into small equilibrium volumes in which thermodynamic potentials and their derivatives are defined. Consider two such volumes designated 1 and 2 (Fig. 4). The pores in the left-hand volume are labeled by index i_1 and those in the right-hand volume by index i_2 . For the occupation numbers of the pores $v_i(\mu)$ we adopt the approximation of local equilibrium (3.9). The expression for the flux through a unit area at the boundary between the locally equilibrium volumes 1 and 2 has the form

$$J = 2 \sum_{i_1, i_2} \left[\frac{v_{i_1}(\mu_1) q_{i_2}(\mu_2)}{\tau_{i_1}} f_{i_1 i_2} \exp(-\beta V_{i_1 i_2}) - \frac{v_{i_2}(\mu_2) q_{i_1}(\mu_1)}{\tau_{i_2}} f_{i_2 i_1} \exp(-\beta V_{i_2 i_1}) \right], \quad (4.1)$$

where $\mu_{1(2)}$ are the chemical potentials in the 1st (2nd) locally equilibrium volumes, respectively; $\tau_{i_{1(2)}}$ are the periods of thermal vibrations of hydrogen atoms in pores, which further are assumed to be equal to a certain average value $\bar{\tau}$; $q_{i_{1(2)}} = 1 - v_{i_{1(2)}}$ is the probability that the pore $i_{1(2)}$ contains no hydrogen atoms; $f_{i_1 i_2}$ is the probability that the jump that begins in pore i_1 is terminated in pore i_2 (this magnitude may

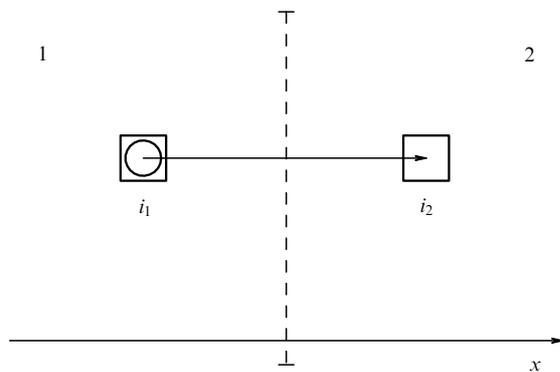


Figure 4. Two locally equilibrium volumes separated by a flat boundary.

be considered to be equal to approximately $1/\bar{z}$, where \bar{z} is the first coordination number in the sublattice of interstices); $V_{i_1 i_2}$ is the energy of activation for the $i_1 \rightarrow i_2$ transition; and the ‘hat’ over the summation sign means that the summation is carried out on a unit area only over those (quasi) interstices between which hydrogen atoms can make jumps.

If we approximate the change in the chemical potential between locally equilibrium elementary volumes by a linear dependence

$$\mu_2 = \mu_1 + l \frac{d\mu}{dx}, \quad (4.2)$$

where l is the characteristic size of the locally equilibrium volume, which is usually accepted to be equal to the length of a diffusion jump of a hydrogen atom [17], we obtain

$$J = -\frac{2\beta l}{\bar{\tau}\bar{z}} \frac{d\mu}{dx} \sum_{i_1, i_2} [v_{i_1} v_{i_2} q_{i_2} \exp(-\beta V_{i_1 i_2}) - q_{i_1} q_{i_2} v_{i_2} \exp(-\beta V_{i_2 i_1})]. \quad (4.3)$$

This expression, which is valid only for a statistically uniform medium, represents a particular case of the kinetic equation of nonequilibrium thermodynamics — the relationship between the macroscopic flux and gradient of the potential [33], and the coefficient $d\mu/dx$ has the meaning of a transport coefficient.

Let the quasi-interstices have a characteristic (or a set of characteristics, which will be detailed below) χ , and the activation energy for the $i_1(\chi) \rightarrow i_2(\chi')$ hydrogen-atom jump depends *only* on the types of pores i_1 and i_2 . Then, we may introduce averaging over all types of pores into Eqn (4.3), which is written in the form of a sum

$$J = -\frac{2A\beta}{\bar{\tau}\bar{z}} \frac{d\mu}{dx} \sum_{\chi, \chi'} f(\chi, \chi') v_\chi q_{\chi'} [q_\chi + v_{\chi'}] \times \exp\{-\beta V(\chi, \chi')\}, \quad (4.4)$$

where A is the average number of ‘interconnected’ pairs of quasi-interstices per unit area of the cross section of the sample and $f(\chi, \chi')$ is the pair distribution function for pore types with the properties

$$f(\chi, \chi') = f(\chi', \chi), \quad \sum_{\chi, \chi'} f(\chi, \chi') = 1. \quad (4.5)$$

The relative concentration $C = c/M$ (M is the number of pores per unit volume) is defined by the expression

$$C = \sum_{\chi} f(\chi) v_\chi, \quad f(\chi) = \sum_{\chi'} f(\chi, \chi'), \quad (4.6)$$

and the expression for the occupation of pores (3.9) has in this case the form

$$v_\chi = \frac{1}{1 + \exp\{\beta(\epsilon_\chi - \mu)\}}. \quad (4.7)$$

Expression (4.4) with allowance for (4.6) and (4.7) reduces to Fick’s first law (2.1); hence, we obtain the following general expression for the diffusion coefficient:

$$D_{ch} = \frac{2Al}{\bar{\tau}\bar{z}M} \frac{\sum_{\chi, \chi'} f(\chi, \chi') \exp\{-\beta V(\chi, \chi')\} v_\chi q_{\chi'} [v_{\chi'} + q_\chi]}{\sum_{\chi} f(\chi) v_\chi q_\chi}, \quad (4.8)$$

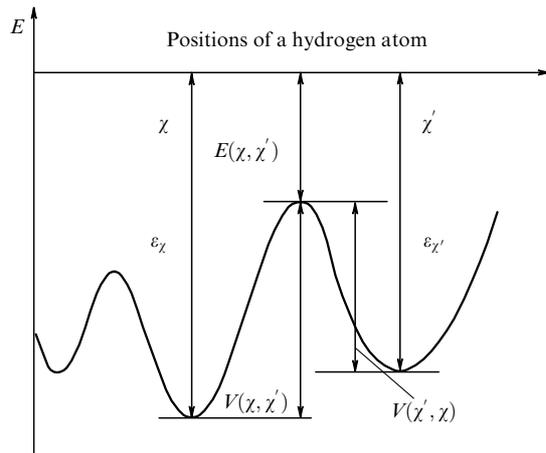


Figure 5. Potential relief for a hydrogen atom.

in which all the information on the structure of the material is contained in the function $f(\chi, \chi')$ and the information on the potential relief is in the quantities ε_χ and $V(\chi, \chi')$.

The calculation of the diffusion coefficient (4.8) requires the knowledge of energetic parameters ε_χ and $V(\chi, \chi')$ (Fig. 5). The exact knowledge of the preexponential factor and its concentration dependence is not of very large importance. The other quantities can be determined from additional experiments, as was made, e.g., in Ref. [61]. However, the interpretation of these experiments requires in its turn the use of sufficiently rough model assumptions. In terms of the same assumptions, it is possible to express the energetic parameters of the problem via the corresponding parameters of the alloy components. Thus, the energies $V(\chi, \chi')$ (Fig. 5) can be represented as

$$V(\chi, \chi') = -\varepsilon_\chi + E(\chi, \chi'), \quad (4.9)$$

where $E(\chi, \chi')$ is the energy at the saddle point that separates configurations with numbers χ and χ' . The calculation of the energy $E(\chi, \chi')$ is a very complex problem. However, the computer calculations [80, 81] show that we may assume with good accuracy that the energy at the saddle point is a constant independent of the concentration, i.e., $E(\chi, \chi') = E_0$. Now, we concretize this problem for various types of disorder.

Crystalline disordered alloys. Consider a binary alloy $A_x B_{1-x}$ ($A_x B_y$) with an infinite solubility. Let the configuration of the χ type be characterized by a atoms A and $b = h - a$ atoms B ($h = 4$ for the tetrapores and $h = 6$ for octapores) and let χ be equal to a ($0 \leq a \leq h$). Then, the diffusion coefficient (4.8) can be expressed through the coefficients of diffusion in pure metals:

$$D_L = \frac{2Al}{\bar{z}M} \exp(-\beta E_0) \exp(\beta \varepsilon_L), \quad L = A, B, \quad (4.10)$$

since in the approximation of a pairwise interaction of hydrogen atoms with the nearest matrix atoms the quantities ε_a have a simple relation to the energies ε_L in pure metals:

$$\varepsilon_a = \frac{1}{h}(a\varepsilon_A + b\varepsilon_B). \quad (4.11)$$

Then, expression (4.8) can be represented in the form of a configuration sum

$$D_{\text{ch}}(C) = D_B \frac{\sum_{a,a'=0}^h m_a P_{aa'} (D_A/D_B)^{a/h} v_a q_{a'} (q_a + v_{a'})}{\sum_{a=0}^h m_a v_a q_a}, \quad (4.12)$$

where m_a is the probability of finding a pore of type a , $P_{aa'}$ is the conditional probability of finding an interstice of type a' near a pore of type a , and v_a are the occupation of interstices (4.7) determined by the expression

$$v_a = \frac{1}{1 + \exp(-\beta \mu') (D_A/D_B)^{a/h}}, \quad (4.13)$$

where μ' is the chemical potential renormalized by a constant factor. To separate the dependence on the hydrogen concentration on the right-hand side of Eqn (4.12), we should take into account the normalization conditions, which permit one to determine μ' :

$$\sum_{a=0}^h m_a v_a = C, \quad \sum_{a=0}^h m_a = 1. \quad (4.14)$$

The dependence on the alloy composition x is found most simply in the regular-solution approximation. Then, m_a is written as a binomial distribution

$$m_a = C_h^a x^a (1-x)^{h-a}, \quad (4.15)$$

and the conditional probabilities $P_{aa'}$ are determined by enumeration of all possible configurations of two neighboring interstices, taking into account that three (in the bcc lattice) or two (in the fcc lattice) sites are common for both interstices (usually, it is assumed that $P_{aa'} = m_{a'}$ [27], which is incorrect). It is seen from, e.g., Fig. 6 that $P_{60} = 0$; i.e., neighboring interstices cannot be surrounded with six atoms of one element and with six atoms of the other element. The correlations are even stronger for the case of tetrapores in the bcc lattice (Fig. 7).

$$P_{aa'}^{bcc} = \frac{1}{4} [x(a\delta_{a,a'} + b\delta_{a,a'+1}) + y(a\delta_{a,a'-1} + b\delta_{a,a'})],$$

$$P_{aa'}^{fcc} = \frac{4}{5} \frac{x^{a'-2} y^{a'-2}}{a'!(6-a')!} [aa'(a-1)(a'-1)y^2 + 2aa'(6-a)(6-a')xy + (6-a)(6-a')(5-a)(5-a')x^2]. \quad (4.16)$$

Set of equations (4.12)–(4.16) is a complete set for the determination of the diffusion coefficient in a disordered binary alloy $A_x B_y$ and its temperature and concentration

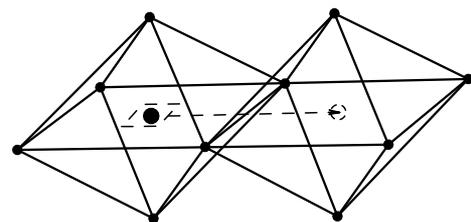


Figure 6. Configuration consisting of two neighboring octahedral pores in an fcc lattice.

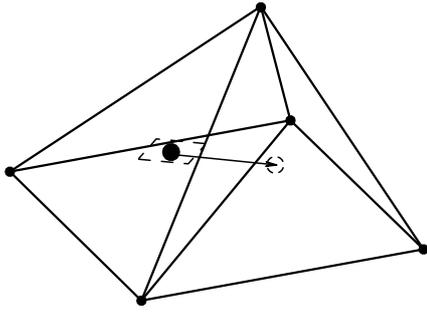


Figure 7. Configuration consisting of two neighboring tetrahedral pores in an fcc lattice.

dependences; the coefficients of diffusion in pure metals serve as parameters of the problem.

The above approach was extended to the case of ternary disordered alloys $A_xB_yC_z$ ($z = 1 - x - y$) [73, 74]. The traditional method of calculation of the hydrogen diffusion coefficient is virtually inapplicable in this case because of the large number of unknown parameters; therefore, the method suggested in [73, 74] is the only suitable method permitting the analysis of the concentration dependences of the hydrogen-diffusion coefficient.

In this case, it is convenient to pass to a two-index system of designations according to the following rule: $\chi \rightarrow ab$ ($0 \leq a \leq h$, $0 \leq b \leq h - a$). Taking into account that

$$\varepsilon_{ab} = \frac{1}{h} [a\varepsilon_A + b\varepsilon_B + (h - a - b)\varepsilon_C], \quad (4.17)$$

we can write Eqn (4.8) in the form of a configuration sum

$$D_{ch}(C) = D_C \left\{ \left[\sum_{a=0}^h \sum_{b=0}^{h-a} \left(\frac{D_A}{D_C} \right)^{a/h} \left(\frac{D_B}{D_C} \right)^{b/h} m_{ab} v_{ab} \right. \right. \\ \left. \left. \times \sum_{a'=0}^h \sum_{b'=0}^{h-a'} P_{ab, a'b'} q_{a'b'} (q_{ab} + v_{a'b'}) \right] \right. \\ \left. \times \left[\sum_{a=0}^h \sum_{b=0}^{h-a} m_{ab} v_{ab} q_{ab} \right]^{-1} \right\}, \quad (4.18)$$

where

$$v_{ab} = \frac{1}{1 + \exp(-\beta\mu') (D_A/D_C)^{a/h} (D_B/D_C)^{b/h}}. \quad (4.19)$$

The concentration dependences $D(C; x, y, z)$ will enter via the quantities

$$m_{ab} = \frac{h!}{a!b!c!} x^a y^b z^c, \quad (4.20)$$

and the conditional probabilities $P_{ab, a'b'}$ [73]

$$P_{ab, ac'b'}^{bcc} = \frac{1}{4} [x(a\delta_{a', a-1}\delta_{b'b} + b\delta_{a', a+1}\delta_{b', b-1} + c\delta_{a', a+1}\delta_{b'b}) \\ + y(a\delta_{a', a-1}\delta_{b'b} + b\delta_{a', a}\delta_{b'b} + c\delta_{a', a}\delta_{b', b+1}) \\ + z(a\delta_{a', a-1}\delta_{b'b} + b\delta_{a', a}\delta_{b', b-1} + c\delta_{a', a}\delta_{b'b})], \\ P_{ab, a'b'}^{fcc} = \frac{4}{5} \frac{1}{a!b!c!} [aa'(a-1)(a'-1)x^{a'-2}y^{b'}z^{c'} \\ + bb'(b-1)(b'-1)x^a y^{b'-2}z^{c'} \\ + cc'(c-1)(c'-1)x^a y^{b'}z^{c'-2} \\ + 2aba'b'x^{a'-1}y^{b'-1}z^{c'} + 2cc'bb'x^a y^{b'-1}z^{c'-1} \\ + 2cc'aa'x^{a'-1}y^{b'}z^{c'-1}]. \quad (4.21)$$

Equations (4.18)–(4.21) completely determine the hydrogen-diffusion coefficient and its concentration dependences in ternary disordered bcc and fcc alloys. The problem in this case is in principle by no means more complex than in the case of binary alloys.

Allowance for short-range order in alloys. The above approach based on the theory of regular solid solutions [82] permits one to take into account the presence of short-range order in alloys. For binary alloys the allowance for short-range order reduces to a redefinition of probabilistic quantities m_a and $P_{aa'}$; the general expression (4.12) remains in this case unaltered. The procedure of the calculation of these quantities is given in [74]. In the final account, they are expressed through the correlation factors G_{LM} :

$$G_{AA} = 1 - 2(1-x)^2\lambda, \quad G_{BB} = 1 - 2x^2\lambda, \\ G_{AB} = 1 + 2x(1-x)\lambda, \\ \lambda = \frac{W}{kT}, \quad W = \left[\frac{1}{2} (V_{AA} + V_{BB}) - V_{AB} \right], \quad (4.22)$$

where W is the energy of mixing in the alloy and V_{LM} are the energies of pairwise interaction of nearest-neighbor atoms of type L and M. In this approximation, the fraction of interstices that have in their neighborhood a atoms of type A and $b = h - a$ atoms of type B is equal to

$$m_a = \frac{(h-2)!}{a!b!} \mu_a x^a y^b, \quad \mu_a = \mu_a^{(1)} + \mu_a^{(2)}, \\ \mu_a^{(1)} = a(a-1)G_{AA}^{a-2}G_{AB}^b + abG_{AA}^{a-1}G_{AB}^{b-1}, \\ \mu_a^{(2)} = b(b-1)G_{BB}^{b-2}G_{AB}^a + abG_{BB}^{b-1}G_{AB}^{a-1}. \quad (4.23)$$

To find the conditional probability $P_{aa'}$, statistical calculations were performed separately for octahedral and tetrahedral pores. For the tetrapores in the bcc lattice, the following expression was obtained:

$$P_{aa'}^{bcc} = \frac{\mu_a^{(1)}(x\delta_{a, a'} + y\delta_{a, a'+1}) + \mu_a^{(2)}(y\delta_{a, a'} + x\delta_{a, a'-1})}{\mu_a}. \quad (4.24)$$

A similar expression for octapores in the fcc lattice has a more complex form:

$$P_{aa'}^{fcc} = \frac{3x^{a'-2}y^{b'-2}}{2a!b!c!} \left\{ a(a-1)a'(a'-1)(1-x)^2 G_{AA}^{(a+a'-5)} \right. \\ \times G_{AB}^{(b+b'-2)} [bG_{AA} + (a-2)G_{AB}] \\ \times [b'G_{AA} + (a'-2)G_{AB}] + aba'b'x(1-x) \\ \times [G_{AA}^{(a+a'-4)} G_{AB}^{(b+b'-3)} ((b-1)G_{AA} + (a-1)G_{AB}) \\ \times ((b'-1)G_{AA} + (a'-1)G_{AB}) + G_{BB}^{(b+b'-4)} G_{AB}^{(a+a'-3)} \\ \times ((a-1)G_{BB} + (b-1)G_{AB}) \\ \times ((a'-1)G_{BB} + (b'-1)G_{AB})] \\ \left. + b(b-1)b'(b'-1)x^2 G_{BB}^{(b+b'-5)} G_{AB}^{(a+a'-2)} \right. \\ \left. \times (aG_{BB} + (b-2)G_{AB})(a'G_{BB} + (b'-2)G_{AB}) \right\}. \quad (4.25)$$

It can easily be checked that, in the absence of correlation, Eqns (4.23)–(4.25) turn into (4.15) and (4.16).

Comparison with experiment. When analyzing diffusion mobility of hydrogen atoms in alloys, expression of the (4.8) type is usually employed, as was, e.g., made in Ref. [61], where the temperature dependence of the diffusion coefficient in bcc $\text{Nb}_{1-y}\text{V}_y$ alloys was studied. In this approach, a large number of parameters of the problem should be known, some of which are determined from additional experiments performed for a given series of alloys; for some alloys, a linear interpolation of diffusion data obtained for pure metals is used. Thus, the values of the energies ε_a and the fractions of configurations m_a are derived from an analysis of P – C isotherms using the nearest-neighbor approximation with respect to the interaction of hydrogen atoms with alloy atoms [83]. The energy of interaction of hydrogen atoms with each other and the magnitude of the preexponential factor are determined assuming that they are linearly dependent on the concentrations of the alloy components. For magnetic alloys of the Fe–Pd type, special methods of determining activation-energy distribution exist [84].

It was shown in our previous work that in virtually the same approximations that were used in Ref. [61] the diffusion coefficient in binary alloys can be expressed through the coefficient of diffusion of pure components and related configuration sum. Such a calculation was performed for concentrated alloys of palladium with platinum [72], whose diffusion coefficients were determined experimentally in [85].

Figure 8 displays the calculated and experimental dependences of the hydrogen diffusion coefficient on the concentration of platinum in Pd–Pt alloys at low hydrogen concentrations ($\beta\mu'(C) \ll 1$), which show that Eqn (4.13) satisfactorily describes experimental data.

The dependence of the diffusion coefficient on the concentration of rhodium in palladium (Fig. 9) is significantly worse described by the theory, apparently due to the fact that Eqn (4.13) does not take into account mutual interaction of hydrogen atoms and the change in this interaction with increasing rhodium concentration. Thus, if we take into account in Eqn (4.7) the interaction of hydrogen atoms between themselves, using it as an adjustable parameter, then the agreement of the theory and experiment, as is seen from Fig. 9, becomes good.

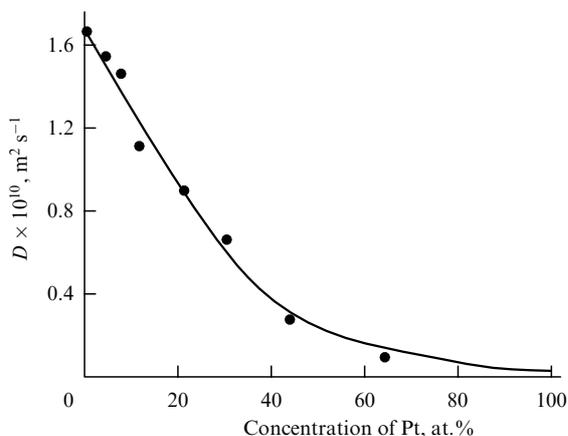


Figure 8. Calculated and experimental dependences of the hydrogen diffusion coefficient on the concentration of Pt in Pd–Pt alloys at $T = 357$ K. Solid line, calculation at $\mu = 0$; solid circles, experimental data [85].

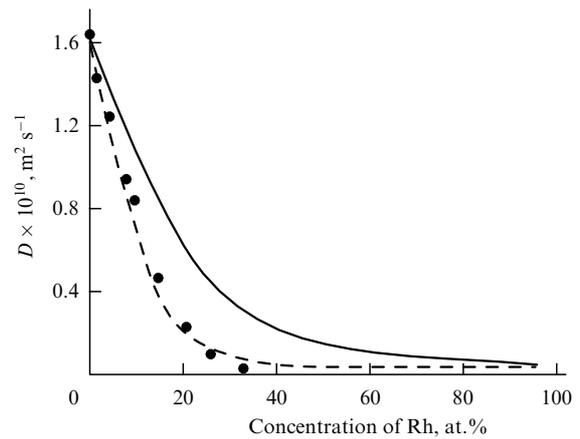


Figure 9. Calculated and experimental dependences of the hydrogen diffusion coefficient on the concentration of Rh in Pd–Rh alloys at $T = 357$ K. Solid line, calculation at $\mu = 0$; dashed line, calculation with allowance for the interaction between hydrogen atoms in the form $\beta f = 0.3 + 12(1 - y)$; solid circles, experimental data [85].

The concentration dependences of hydrogen diffusion coefficient were also calculated for bcc Nb–Ta alloys (Fig. 10) and Nb–V alloys (Fig. 11). The experimental data were taken from Refs [86, 87]. It is seen that the agreement between the calculated and experimental data for the Nb–Ta alloys is satisfactory, whereas for the Nb–V alloys experiment yields lower values of $D(C)$ in a wide range of vanadium concentrations. This can be due to the dependence of the prefactor for these alloys on their chemical composition, which was neglected in calculations.

Note that the approach developed in Ref. [75] did not take into account the possible variation of the electron structure of the base metal upon alloying. Meanwhile, it was conclusively shown in [36] in the example of a wide class of binary palladium alloys (Pd–Ag, Pd–Au, Pd–In, Pd–Cd, Pd–Y, Pd–Ti, etc.) that there exists a correlation between the magnitude of the hydrogen diffusion coefficient and the concentration of valence electrons of the alloying element. This effect clearly manifests itself just for the palladium-based alloys because of the small width of its d band [11, Vol. 2, Ch. 3].

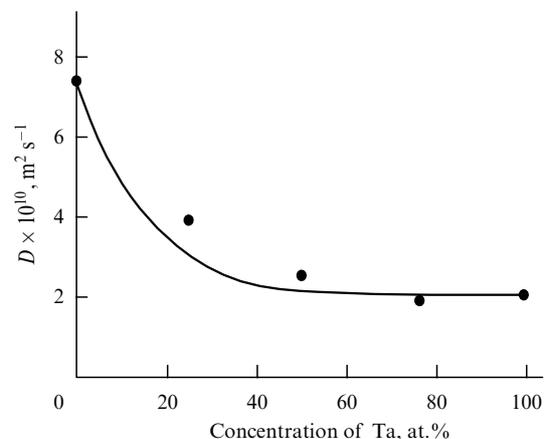


Figure 10. Calculated and experimental dependences of the hydrogen diffusion coefficient on the concentration of Ta in Pd–Ta alloys at $T = 296$ K. Solid line, calculation; solid circles, experimental data [87].

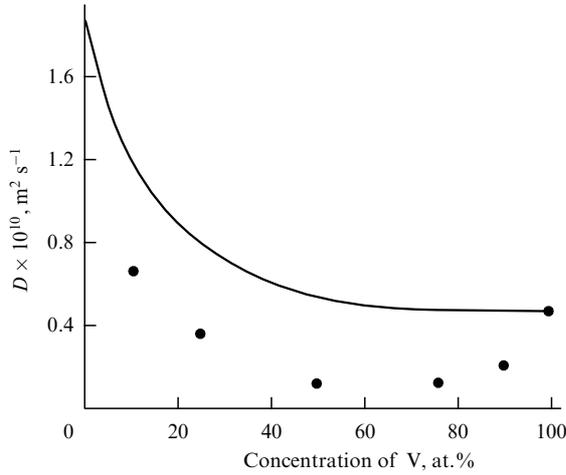


Figure 11. Calculated and experimental dependences of the hydrogen diffusion coefficient on the concentration of V in Nb–V alloys at $T = 296$ K. Solid line, calculation at $\mu = 0$; solid circles, experimental data [87].

Dependences of the hydrogen diffusion coefficient on the composition of ternary disordered alloys $V_xTa_yNb_{1-x-y}$ with a bcc lattice and $Pd_xAg_yPt_{1-x-y}$ with an fcc lattice were also calculated [74].

The results of the calculations are given in Figs 12 and 13. It is seen that the diffusion coefficient in ternary alloys changes nonlinearly with composition. As was shown by corresponding calculations, the allowance for short-range order in the adopted approximation only weakly affects the diffusion coefficient of both binary and ternary alloys. The diffusion data for pure components were borrowed from Ref. [88].

Amorphous alloys. Disordered crystalline systems, including amorphous alloys, are characterized by the notion of free volume. This means that the average atomic volume in an amorphous material may be somewhat greater than in a crystal [89]. The free volume in amorphous samples is distributed statistically in the form of local distortions of crystal lattice. This permits one to characterize quasi-interstices by two parameters: the first parameter determines the chemical surroundings of a hydrogen atom with matrix

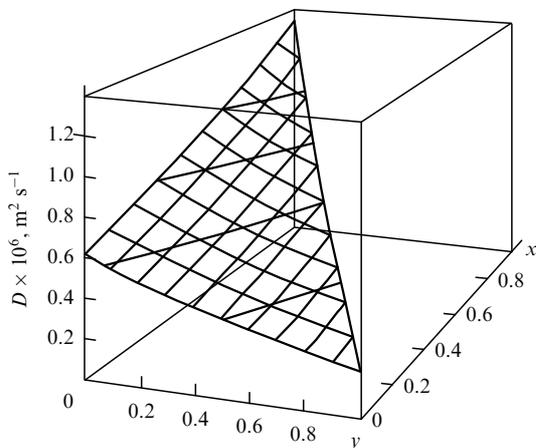


Figure 12. Diffusion coefficient of hydrogen in bcc $V_xTa_yNb_{1-x-y}$ alloys at $T = 600$ K.

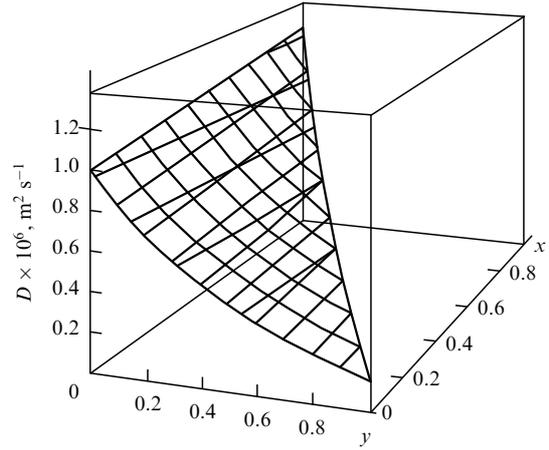


Figure 13. Diffusion coefficient of hydrogen in fcc $Pd_xAu_yPt_{1-x-y}$ alloys at $T = 800$ K.

atoms; the second parameter shows the degree of the distortion of the pore as compared to the interstice of an ideal crystal. In Refs [75, 76], we took the microscopic dilatation α — the relative change in the pore volume as compared to the crystal interstice — as the second parameter. An analogous idea was earlier used in Ref. [65] for the calculation of the activation-energy distributions for the diffusion of interstitial impurities in amorphous metals.

In Eqns (4.5)–(4.8), a substitution $\chi \rightarrow (i, \alpha)$ was made. Summation over all possible types of pores i in these equations should be understood as summation over the chemical configurations of the pores, to which integration over dilatations α is added.

Neglecting correlations between the dilatation of a pore and the type of its surroundings, we have

$$f(\chi, \chi') = f_{ij}(\alpha, \alpha') = W(\alpha, \alpha') m_i P_{ij},$$

$$f(\chi) = f_i(\alpha) = W(\alpha) m_i, \tag{4.26}$$

where $W(\alpha, \alpha')$ is the pair pore distribution function; $W(\alpha)$ is the single pore distribution function; and m_i and P_{ij} are the analogs of m_a and $P_{aa'}$. The quantities introduced possess the following properties:

$$W(\alpha, \alpha') = W(\alpha', \alpha), \quad m_i P_{ij} = m_j P_{ji},$$

$$\int W(\alpha, \alpha') d\alpha' = W(\alpha), \quad \sum_i m_i P_{ij} = m_j, \tag{4.27}$$

$$\iint W(\alpha, \alpha') d\alpha d\alpha' = 1, \quad \sum_{i,j} m_i P_{ij} = 1.$$

The values of m_i and P_{ij} for binary alloys are determined by Eqns (4.15) and (4.16), respectively.

It was supposed that the function $W(\alpha)$ has the form of a Gaussian distribution:

$$W(\alpha) = \frac{1}{\sqrt{2\pi p}} \exp\left(-\frac{\alpha^2}{2p}\right), \tag{4.28}$$

where it is assumed that $\langle \alpha \rangle = 0$, since its magnitude in amorphous systems is of the order of a few percent [89].

The pair pore distribution function $W(\alpha, \alpha')$ carries additional information on the correlation between neighboring pores. In the absence of correlation, we have

$W(\alpha, \alpha') = W(\alpha) W(\alpha')$. With allowance for the pore correlation, we obtain

$$W(\alpha, \alpha') \cong W(\alpha) W(\alpha')(1 - 2Q\alpha\alpha'), \quad (4.29)$$

where Q is the correlation factor. If $Q < 0$, then the pores that have dilatations of the same sign will be ‘attracted’ to one another, forming a structure of diffusion paths. The value $Q > 0$ corresponds to ‘intermixing’ of pores with dilatations of opposite signs. In this case the amorphous material will be uniform on a mesoscopic scale. Assuming that distribution (4.28) is sufficiently narrow, we can pass from Eqn (4.29) to a generalized Gaussian distribution

$$W(\alpha, \alpha') = \frac{\sqrt{P^2 - Q^2}}{\pi} \exp \left\{ -P[(\alpha)^2 + (\alpha')^2] - 2Q\alpha\alpha' \right\}. \quad (4.30)$$

Here, $p = P/2(P^2 - Q^2)$.

In Refs [75, 76], a relation was established between the distribution function $W(\alpha)$ for an amorphous alloy produced from an fcc alloy with the parameters of the radial atomic distribution function $g(r)$ determined from X-ray and neutron diffraction experiments [90]:

$$\begin{aligned} W(\alpha) &= \frac{d}{Z_1 Z_2} \int_{u^*(\alpha)}^{u^{**}(\alpha)} du_1 g(r_1 + u_1) g(r_2 + \alpha d - 2\sqrt{2}u_1), \\ u^* &= \max \left(-r_1, \frac{d(1 + \alpha) - r^{**}}{\sqrt{2}} \right), \\ u^{**} &= \min \left(r^* - r_1, \frac{d(1 + \alpha) - r^*}{2\sqrt{2}} \right), \\ \int_0^{r^*} dr g(r) &= Z_1, \quad \int_{r^*}^{r^{**}} dr g(r) = Z_2, \end{aligned} \quad (4.31)$$

where $Z_1 = 12$ and $Z_2 = 6$ are the first and second coordination numbers, respectively; d is the lattice parameter; and r_1 and r_2 are the radii of the first and second coordination shells, respectively. When the $g(r)$ function is approximated by a Gaussian, for the distribution function we obtain Eqn (4.28) with a parameter

$$p = \frac{8\sigma_1^2 + \sigma_2^2}{d^2}, \quad (4.32)$$

where σ_1 and σ_2 are the half-widths of the first and second peaks of the radial distribution function, respectively.

Note that a more general approach [77] based on lattice theories [91] shows that the quantities are related to the characteristics of not only radial but also angular distribution of amorphous-matrix atoms.

To calculate the diffusion coefficient, it was assumed (see Fig. 5) that

$$V_{ij}(\alpha, \alpha') = -\varepsilon_i(\alpha) + E(\alpha, \alpha'), \quad (4.33)$$

where, neglecting a change in the pore volume occurring when a hydrogen atom is placed into it and at $\alpha \ll 1$, we have

$$\varepsilon_i(\alpha) = \varepsilon_{i0} + \delta_i \alpha^2. \quad (4.34)$$

At the saddle point, the hydrogen atom pushes away nearest-neighbor metal atoms; therefore, compression leads to an

increase in its energy and tension results in a decrease in its energy. The quantities α and α' should enter into the expression for $E(\alpha, \alpha')$ in a symmetric way, since each initial pair of interstices is symmetric with respect to the saddle point. Hence, we have

$$E(\alpha, \alpha') = E_0 - \omega(\alpha + \alpha'), \quad (4.35)$$

where the quantities δ_i and $\omega > 0$ are the parameters of the theory, and the quantities ε_{i0} and E_0 refer to the undistorted (crystal) state of the alloy.

As a result, the diffusion coefficient (4.8) is now written as

$$\begin{aligned} D_{\text{ch}} &= \frac{2Al}{\bar{v}zM} \\ &\times \left\{ \left[\sum_{i,j} m_i P_{ij} \langle \langle S_{ij}(\alpha, \alpha') \exp[\beta(\omega(\alpha + \alpha') + \delta_i \alpha^2)] \rangle \rangle \right] \right. \\ &\times \exp[\beta(\varepsilon_{i0} - E_0)] \left. \left[\sum_i m_i \langle v_i(\alpha) q_i(\alpha) \rangle \right]^{-1} \right\}, \quad (4.36) \end{aligned}$$

$$S_{ij}(\alpha, \alpha') = v_i(\alpha) q_j(\alpha') [q_i(\alpha) + v_j(\alpha')],$$

where double angular brackets $\langle \langle \dots \rangle \rangle$ mean averaging with a pair pore distribution function $W(\alpha, \alpha')$, whereas single angular brackets correspond to the distribution function $W(\alpha)$. The formula for the pore occupation numbers (4.7) is modified to become

$$v_i(\alpha) = \frac{1}{1 + \exp\{\beta(\varepsilon_{i0} + \delta_i \alpha^2 - \mu)\}}, \quad (4.37)$$

and Eqn (4.6) relating the chemical potential to the concentration of hydrogen atoms has the form

$$C = \sum_i m_i \langle v_i(\alpha) \rangle. \quad (4.38)$$

The use of Gaussian distributions (4.28) and (4.30) for the functions $W(\alpha)$ and $W(\alpha, \alpha')$ permits one to obtain an analytical expression for the hydrogen diffusion coefficient in alloys [77]. At small concentrations C , it has a simple form (the effects of pore correlation manifest themselves beginning from terms that are quadratic in concentration, C^2)

$$\begin{aligned} D_{\text{ch}} &= \frac{2Al}{\bar{v}zM} \frac{\exp[-\beta E_0 + (1/2)\Omega(1 - \vartheta)]}{H_1} \\ &\times \left\{ 1 + 2 \frac{C}{H_1} \left(\frac{H_2}{H_1} - \Phi_1 \right) \right. \\ &\left. + \frac{C^2}{H_1^2} \left[\frac{6H_2}{H_1} \left(\frac{H_2}{H_1} - \Phi_1 \right) + 2\Phi_2 - \frac{3H_3}{H_1} + \varkappa \right] \right\}, \quad (4.39) \end{aligned}$$

where

$$\begin{aligned} H_x &= \sum_i \frac{m_i}{(y_i)^x \sqrt{1 + x\Delta_i}}, \\ \Phi_x &= \sum_j \frac{m_j}{(y_j)^x \sqrt{1 + x\Delta_j}} \exp\left(-\frac{1}{4}\Omega(1 - \vartheta)^2 \frac{x\Delta_j}{1 + x\Delta_j}\right), \\ \varkappa &= \sum_{i,j} \frac{m_i P_{ij}}{y_i y_j \sqrt{(1 + \Delta_i)(1 + \Delta_j) - \vartheta^2 \Delta_i \Delta_j}} \\ &\times \exp\left[-\frac{1}{4}\Omega(1 - \vartheta)^2 \frac{\Delta_i + \Delta_j + 2(1 + \vartheta)\Delta_i \Delta_j}{(1 + \Delta_i)(1 + \Delta_j) - \vartheta^2 \Delta_i \Delta_j}\right], \end{aligned}$$

$\Omega = 2\beta^2\omega^2p$, $\Delta_i = 2\beta\delta_i p$, $y_i = \exp(\beta\varepsilon_{i0})$, and $\vartheta = Q/P$ is the degree of pore correlation.

Let us analyze the temperature dependence of the diffusion coefficient D_{ch} . If the dispersion of hydrogen-atom energies in various interstices is small, $\beta \max|\varepsilon_{i0} - \bar{\varepsilon}| < 1$, where $\bar{\varepsilon}$ is the average energy of a hydrogen atom in an interstice, the temperature dependence of D_{ch} is mainly determined by the term in (4.39) that is of zero order in concentration. We may introduce the effective activation energy for chemical diffusion of hydrogen in an amorphous alloy, which is equal to

$$Q_{\text{eff}} = -\frac{d \ln D_{\text{ch}}}{d\beta} \approx \mathfrak{Q} - 2\beta\omega^2p(1 - \vartheta), \quad (4.40)$$

where $\mathfrak{Q} = E_0 - \bar{\varepsilon} - 2\omega(\alpha)$. Note that it follows from Eqn (3.4) obtained by the random-walk method that the effective energy of activation for diffusion in amorphous materials, in contrast to crystalline materials, should change linearly with reciprocal temperature. The rate of this change is determined by the parameter ω that characterizes the disorder in the saddle point energies. Q_{eff} depends also on the degree of pore correlation: the tendency of pores with dilatations of the same sign to group together ($\vartheta < 0$) enhances the dependence of the effective activation energy on temperature, whereas the intermixing of pores with dilatations of different signs ($\vartheta > 0$) weakens this dependence.

Figure 14 displays the temperature dependence of the effective activation energy for hydrogen diffusion in a metallic glass (TiCu)H_{1.3-1.35} taken from the review [19]. The last three points fall well onto the straight line $Q_{\text{eff}} \approx (28 - 3100/T(\text{K})) \text{ kJ mol}^{-1}$ (the outlying first point apparently is due to the effect of structural relaxation). A comparison of the characteristics of this curve with Eqn (4.40) yields $\mathfrak{Q} \approx 0.3 \text{ eV}$ and $\omega\sqrt{p} \approx 0.04 \text{ eV}$ (at $\vartheta = 0$).

The activation energy for hydrogen diffusion in the crystalline alloy (CuTi)H_{0.94} is equal to $\sim 0.8 \text{ eV}$ [92]. This indicates that this approach at reasonable values of the parameters is capable of explaining the temperature behavior of the hydrogen-diffusion coefficient in amorphous alloys.

Note that in the case of large ‘configurational’ dispersion of hydrogen-atom energies in equilibrium positions, when Eqn (4.40) is invalid (the existence of such situations follows

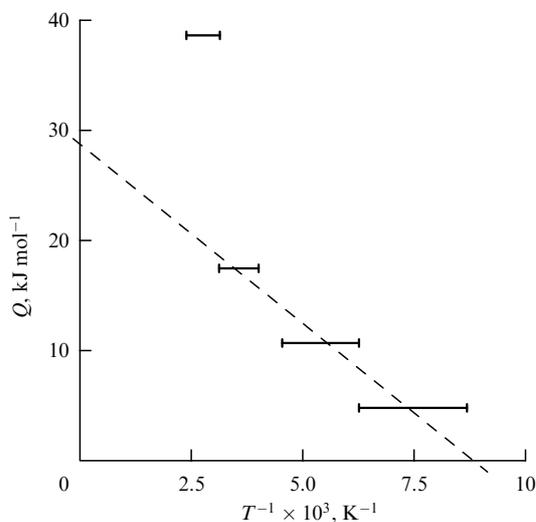


Figure 14. Temperature dependence of the activation energy for hydrogen diffusion in an amorphous alloy (TiCu)H_{1.3-1.35} [19].

from the data of Ref. [32, Ch. 3]), the temperature dependence of the diffusion coefficient proves to be more complex. In this case, it is determined by terms dependent on hydrogen concentration.

The concentration dependence of D_{ch} (4.39) can most simply be analyzed in the case of a metal. Then,

$$D_{\text{ch}} = D(1 + LC + SC^2), \quad (4.41)$$

where

$$D = \frac{2Al}{\bar{\varepsilon}M} \exp \left\{ -\beta(E_0 - \varepsilon_0) + \frac{1}{2}\Omega(1 - \vartheta) \right\} \sqrt{1 + \Delta}, \quad (4.42)$$

and the expansion coefficients have the form

$$\begin{aligned} L &= 2 \left\{ \frac{1 + \Delta}{\sqrt{1 + 2\Delta}} - \exp \left[-\frac{1}{4}\Omega(1 - \vartheta)^2 \frac{\Delta}{1 + \Delta} \right] \right\}, \\ S &= \frac{6(1 + \Delta)}{\sqrt{1 + 2\Delta}} \left\{ \frac{1 + \Delta}{\sqrt{1 + 2\Delta}} - \exp \left[-\frac{1}{4}\Omega(1 - \vartheta)^2 \frac{\Delta}{1 + \Delta} \right] \right\} \\ &+ \frac{2(1 + \Delta)}{\sqrt{1 + 2\Delta}} \exp \left[-\frac{1}{2}\Omega(1 - \vartheta)^2 \frac{\Delta}{1 + 2\Delta} \right] - 3 \frac{(1 + \Delta)^{3/2}}{\sqrt{1 + 3\Delta}} \\ &+ \frac{1 + \Delta}{\sqrt{(1 + \Delta)^2 - \vartheta^2\Delta^2}} \exp \left[-\frac{1}{2}\Omega(1 - \vartheta)^2 \frac{\Delta}{1 + \Delta(1 - \vartheta)} \right]. \end{aligned} \quad (4.43)$$

It is seen from Eqn (4.41) that the transition to the amorphous state leads to an increase in the diffusion coefficient and the appearance of an additional dependence on concentration in it. For metals, this means the appearance of positive first and second derivatives of the diffusion coefficient with respect to concentration in the vicinity of $C = 0$. In amorphous alloys, the behavior will be the same: the diffusion coefficient increases with increasing impurity concentration ($dD_{ch}/dC > 0$, $d^2D_{ch}/dC^2 > 0$). An additional analysis of the coefficients L and S in (4.41) shows that the effect of ‘attraction’ of pores with dilatations of the same sign leads to a significant increase in the diffusion coefficient with increasing hydrogen concentration; the random distribution of pores with dilatations of different signs decreases the diffusion permeability of amorphous materials and weakens its dependence on hydrogen concentration.

Comparison with Kirchheim theory. Now, we compare the above approach with the Kirchheim theory [27] leading to Eqn (3.13) for the diffusion coefficient. To this end, we rewrite expression (4.36) using averaged characteristics:

$$\begin{aligned} D_{\text{ch}} &= D_{\text{hyp}} \beta \exp [\beta(\mu - \bar{\varepsilon})] \\ &\times \sum_{i,j} m_i P_{ij} \langle \langle [1 - v_i(\alpha)][1 - v_j(\alpha')] \rangle \rangle \\ &\times \exp [\beta\omega(\alpha + \alpha' - 2\langle\alpha\rangle)] \frac{\partial\mu}{\partial C}, \end{aligned} \quad (4.44)$$

where

$$D_{\text{hyp}} = \frac{2Al}{\bar{\varepsilon}M} \exp(-\beta\mathfrak{Q})$$

has the same meaning as in Eqn (3.13), and v and μ are determined by Eqns (4.37) and (4.38). In terms of the Kirchheim theory (the constancy of the energy at the saddle point ($\omega = 0$) and neglecting the correlation between the atoms of different types $P_{ij} = m_j$ and pore dilatation

$W(\alpha, \alpha') = W(\alpha)W(\alpha')$, Eqn (4.44) takes on the form

$$D_{\text{ch}} = D_{\text{hyp}} \beta \exp\{\beta(\mu - \bar{\varepsilon})\} (1 - C)^2 \frac{\partial \mu}{\partial C}. \quad (4.45)$$

Formula (4.45) without the factor $(1 - C)^2$ was obtained in [27] for amorphous metals at small hydrogen concentrations. On the assumption that the lattice gas of hydrogen atoms is degenerate, this formula turns into (3.13) provided that $C \ll 1$. Similarly, in terms of the approach considered, we can obtain, at $C \ll 1$ ($\mu < \varepsilon_0$), a simple expression

$$\begin{aligned} D_{\text{ch}} &= D_{\text{hyp}} \exp(-\beta \delta p) \sqrt{1 + 2\beta \delta p} (1 - C)^2 \\ &= \frac{2Al}{\bar{\varepsilon} \bar{z} c_{\text{max}}} \exp[-\beta(E_0 - \varepsilon_0)] \sqrt{1 + 2\beta \delta p} (1 - C)^2. \end{aligned} \quad (4.46)$$

The difference between Eqns (3.13) and (4.46) is explained by the fact that Kirchheim in his work used the Gaussian energy distribution (3.3) with a variation σ determined by Eqn (3.14), whereas if the Gaussian distribution for dilatations (4.28) with allowance for (4.34) is applied, this yields the following form of the effective distribution for the potential energies of hydrogen atoms in quasi-interstices:

$$n(\varepsilon) = \frac{1}{\sqrt{2p\delta\pi(\varepsilon - \varepsilon_0)}} \exp\left\{-\frac{\varepsilon - \varepsilon_0}{2p\delta}\right\}, \quad \varepsilon \in (\varepsilon_0; +\infty), \quad (4.47)$$

where the variation $\langle(\varepsilon - \bar{\varepsilon})^2\rangle^{1/2}$ is equal to $\sqrt{2p\delta}$, and p for alloys with an fcc lattice is given by Eqn (4.32).

Thus, the model discussed in this section is capable of explaining the temperature and concentration dependences of the hydrogen diffusion coefficient in amorphous metals and alloys. Experiment shows that the parameters of the theory have reasonable values.

5. Conclusion

In this review, we discussed experimental data and methods, as well as theoretical approaches, to the problem of hydrogen diffusion in metals and alloy disordered on the atomic and crystalline levels. In our opinion, the concentration dependences can most conveniently be analyzed in research on chemical diffusion. Naturally, to obtain the complete picture of diffusion of interstitial atoms in disordered materials, one should combine different (equilibrium and nonequilibrium) methods of studying hydrogen transport in these systems. Note one specific distinction of the methods of studying hydrogen diffusion: the impossibility of determining the profile of its concentration at a given time moment. The key problems in the investigation of hydrogen diffusion are:

(a) the shape of the potential relief through which hydrogen atoms move in the material and the relation of this shape to the characteristics of the material obtained from other (nondiffusional) experiments;

(b) the relation of the microscopic parameters of motion of impurity atoms (transition frequencies, etc.) to the observed diffusional data; and

(c) comparison of the experimental data on hydrogen diffusion obtained using different experimental techniques.

The main feature of hydrogen diffusion in disordered materials distinguishing them from pure metals and ordered alloys is the variety of energies of positions that can be occupied by hydrogen atoms in these systems. For alloys

with atomic disorder, these are interstices with different surroundings of hydrogen atoms with metal atoms; for systems with crystalline disorder, these are interstices with different surroundings of hydrogen atoms with metal atoms and with interatomic distances fluctuating from one site to another. In view of the complexity of the quantum-mechanical problem of finding the effective potential of metal–hydrogen interaction, the common feature of the majority of work concerning diffusion in alloys with atomic disorder is the development of model assumptions about the form of this potential, which serve as a basis for the calculation of the energies of hydrogen atoms in interstices and saddle points. Thus, Vykhodets et al. [64] applied a Morse potential; Brower et al. [61] used a semi-empirical approach (part of the parameters of the potential relief were determined directly in independent experiments, others were extrapolated because of the lack of experimental data); Biscarini et al. [62] employed another semi-empirical method. For the materials with a crystalline disorder, the situation is even more complicated because of the appearance of an additional distribution of the energies of hydrogen atoms due to fluctuations of interatomic distances in such materials. Such a distribution was first taken into account for the case of amorphous metals by Kirchheim in [27], who assumed that the half-width of this distribution is related to the half-width of the first peak of the radial distribution function of the metal. At present, it is assumed that each peak in the energy distribution in an amorphous alloy related to a different type of hydrogen atom surrounding with metal atoms is broadened into a bell-shaped curve because of the breaking of the long-range order. The question of whether or not such peaks overlap should be solved separately for each concrete disordered material [32]. Analysis performed by Richards [65] showed that the parameters of distribution of hydrogen atoms in different positions in an amorphous metal in the general case may be related to the characteristics of its radial distribution function in a sufficiently simple manner; at the same time, to find the dispersion of the saddle point energies, additional assumptions on the form of the metal–hydrogen interaction potential in such a system are needed.

It is noted in this review that the aim of the majority of theoretical works concerning atomic diffusion in disordered materials is to obtain relationships similar to the Einstein relation or the empirical Fick's first law on the basis of microscopic concepts of the structure of the medium. The parameters of these relationships are identified with the experimentally measured coefficients of tracer diffusion and chemical diffusion. This is the most reliable and direct method of comparison of theory and experiment. However, when studying systems with a complex structure, such as nanocrystalline materials, the realization of this approach meets with large technical difficulties. The existing phenomenological approaches [69] enable one to easily take into account the presence of an advanced microstructure in the disordered material and determine its effect on the transport properties of the medium. The task of prior importance for any theory is, in our opinion, a synthesis of phenomenology with a reliable microscopic approach. One of the first steps in this direction was the work by Hermann et al. [53], which suggested a model for the calculation of the coefficient of Einstein diffusion in a two-component material consisting of a disordered matrix and crystalline inclusions of a regular shape. According to the authors of [53], their model is applicable for determining diffusion coefficients in an arbitrary statistically isotropic

two-component system. At the same time, to confirm the validity of their constructions, they were forced to resort to computer simulation, i.e., their approach also suggests the use of phenomenology that has not been approved microscopically.

One of the unsolved problems is also that of the relation between the data obtained by different experimental methods and, in particular, the problem of the relationship between the Einstein diffusion coefficient and the coefficient of chemical diffusion of hydrogen atoms in metals and alloys with a crystalline disorder. This problem is quite topical, since the available models of disorder used to explain the results of NMR and neutron quasi-elastic scattering experiments in some amorphous alloys (α -Zr₃RhH_{3,5}, Pd_{1-y}Si_yH_x) and the data of electrochemical investigations frequently contradict one another [32, Ch. 3].

In this review, we presented our previously developed approach [72–74] to the calculation of the coefficient of chemical diffusion of hydrogen in binary and ternary alloys with atomic disorder. This approach is based on the summation over pore types (over the types of arrangement of atoms of various kinds around them) for the determination of the flow of impurity atoms and on the hypothesis of a local equilibrium, and in fact is the development of Smirnov's theory [17]. Formally, this approach can be considered as a generalization of the work of Brower et al. [61]. It was shown that in the approximation of hydrogen–metal pairwise interaction and in the absence of interaction of hydrogen atoms with one another, it is sufficient to know only the coefficients of hydrogen diffusion in pure metals and the degree of chemical disorder in the alloy. This approach permits one to describe the dependence of the coefficient of chemical diffusion of hydrogen on the alloy composition, hydrogen concentration, and temperature.

Comparison of calculated and experimentally obtained dependences of the diffusion coefficient on the composition of binary fcc Pd–Pt and Pd–Rh alloys with the bcc Nb–V and Nb–Ta alloys was performed. Unfortunately, we do not know any systematic investigations of the diffusion coefficient in ternary alloys; therefore, it would be quite desirable to perform diffusional experiments in quasi-binary alloys based on Pd.

The approach presented in this review permits one to extend the theory to the calculation of the diffusion coefficient of hydrogen in amorphous materials, whose specificity is taken into account by introducing local dilatation, which reflects the effect of static fluctuations of the volume of quasi-interstices [76, 77]. In terms of the generalized approach, the energies of hydrogen atoms in quasi-interstices and at saddle points are uniquely related to the types and configuration of surrounding metal atoms and to the dilatations of interstices over which hydrogen atoms move in diffusion events. As a result, the diffusion permeability of a material depends on the coefficients of diffusion in pure metals and on the pair distribution function for the volumes of nearest-neighbor quasi-interstices. This function can be approximated by a generalized Gaussian distribution or related to the multiparticle correlation function of static displacements of atoms of the amorphous matrix. The use of the generalized Gaussian distribution makes it possible to obtain explicit expressions for the diffusion coefficients of hydrogen in amorphous metals and alloys to an accuracy of quadratic terms in its concentration and to analyze the effect of the correlation of neighboring pores on the transport properties of amorphous

materials. The expressions obtained satisfactorily explain the concentration and temperature dependences of the diffusion coefficient. It was shown that in the absence of a spatial correlation of the volumes of quasi-interstices, and neglecting changes in the energies of saddle points in amorphous metals, the expression that was found for the diffusion coefficient turns into the corresponding expression found earlier by Kirchheim [27].

In the future, we intend to extend this approach to the description of the process of hydrogen transport in disordered systems with a developed microstructure, e.g., in partially crystalline and nanocrystalline alloys. The most important steps in this direction may be the consideration of multijump rather than single-jump process as an elementary event of diffusion and the discarding of the hypothesis on the existence of local equilibrium; this will permit us to describe various nonstationary regimes of diffusion in disordered systems. The possibility of a theoretical interpretation of nonstationary diffusion experiments in nanocrystalline materials will permit us to obtain additional data on their microscopic and mesoscopic structure. In our opinion, the path to the synthesis of phenomenological and microscopic concepts on the diffusion of interstitial atoms in disordered materials lies precisely in this direction.

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