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Experimental determination of parameters of multichannel hydrogen diffusion in solid probe

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ABSTRACT

The multi-channel diffusion mechanism is modeled by diffusion equations.

The method for analysis of experimental dynamical curves of vacuum hot extraction (VHE) is developed, which allows to determine the binding energy and diffusion constants of hydrogen in the probe under study.

The experimental data have been obtained using industrial hydrogen analyzer, which allows to carry out the absolute measurements of the dynamical curves vacuum hot extraction of the hydrogen from a solid probe. Experimental verification of mathematical models gives adequate results.

The differences of the proposed approach with the method of TDS are discussed.

Introduction

The study of hydrogen diffusion in solids has a great practical importance. The phenomenon of hydrogen fragility and cracking castings in the process of cooling and crystallization occurs as a result of the hydrogen diffusion.

Gorsky [1,2] has proved that apart from temperature and concentration gradient, mechanical tensions arising in deformation of crystal matrix influence diffusion of atoms in solids. This has made it possible to explain the mechanism of the gradual evolution of hydrogen embrittlement in metallic parts, elements and the formation of cold cracks in welds. The hydrogen diffusion plays an important role in the processes of corrosion, cracking and brittle failure [3–8]. The influence of hydrogen on electric properties of semiconductors is also essential [9].

Control of the hydrogen concentration in metals and semiconductors is usually performed in industry [10–12]. Every day, thousands experimental determinations of hydrogen concentration and parameters of its interaction with the solid state matrix are performed in the world. During the test the sample is heated in vacuum or in the flux of an inert gas during this analyses for extraction of the hydrogen.

The flux of hydrogen is measured in such experiments. The study of these fluxes as function of time and temperature allows one to estimate the energy of interaction of hydrogen with the solid state matrix and its defects.

It was established that hydrogen in solids occupied certain energy levels. It was established that hydrogen in solids occupied certain energy levels. It was found that hydrogen with binding energy in the range of 0.2—0.4 eV considerably influences on plasticity and strength of the steels.

Usually for determination of binding energy is used the method of thermo-desorption spectra (TDS). This method is given in Ref. [13]. Extraction of hydrogen from a sample is considered as a chemical reaction of the first order with the activation energy equal to the binding energy. Thus the effect of the hydrogen diffusion inside the studied sample is considered negligible.

On the one hand, this contradicts to the experimental data, since even at relatively small sizes of the sample account for diffusion introduces essential corrections to the values of binding energy [14]. On the other hand, mathematical modeling of the TDS measured experimentally evidences for low accuracy of such approach [15]. As a rule, the hydrogen's binding energies of about 0.2 eV should yield notable hydrogen fluxes at normal conditions, that is not observed experimentally.

It is possible to estimate the binding energy using other methods, e.g. the spectral one [9]; however this method is adequate only in the case of thin samples in the form of films and membranes.

In connection with the strong influence of hydrogen with different binding energies on the structure and strength of materials it becomes necessary to develop approaches which can be used not only in scientific experiments but also in industrial tests.

probe [9,16—19] (Hydrogen Analysis by Vacuum Hot Extraction (VHE). In our experiments we used industrial hydrogen analyzer AV-1 with mass-spectrometric registration of dependence of hydrogen flux from the sample on time, in the process of the sample heating in vacuum. The exterior of the apparatus is shown in Fig. 1(a).

Fig. 1(b) shows the system of probe preparation composed of the extraction system 1, 3 (made of the fused silica) and the radiation furnace 4 whose temperature maintained constant during the analysis. The samples 2 are placed in the cold appendix of extractor 1.

In performing analysis, the sample 2 is thrown off to the analytical Fig. 1 without spoiling of vacuum. The analytical appendix 3 is maintained at a constant temperature of extraction, which is provided by the furnace 4 put on the appendix.

A schematic drawing of the AV-1 is presented in Fig. 2.

For most of the alloys the extraction temperature falls in the range 400—800 °C. The extractor volume is pumped continuously with the analyzer pump down to the working pressure of 100 μPa. The investigated sample is heated slowly up to the extractor temperature. The hydrogen flux from the sample is measured by mass-spectrometric analyzer preliminarily calibrated on the standard hydrogen containing samples or on the gas calibration. As a result, dependence of hydrogen flux from the extractor system on time (the extraction curve) is obtained. An integral of the extraction curve over time is proportional to the amount of hydrogen extracted from the sample. The shape of the curve has features typical for the aluminum, magnesium, titanium alloys and the different marks of steels. In determining the diffusion parameters, we compare the experimental extraction curve to the calculated one obtained by mathematical modeling of the time dependent hydrogen diffusion in the studied sample.

Measurement of hydrogen concentration by vacuum hot extraction method

The vacuum heating method is used both in experiments and in industrial control of hydrogen concentration in a solid

Modeling of diffusion process in sample

Consider the process of the sample heating in vacuum using the titanium samples studied experimentally as examples.
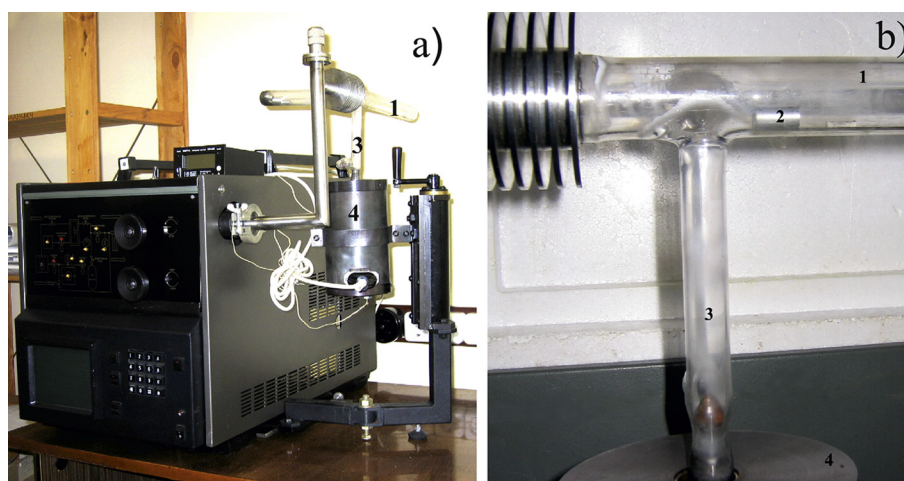

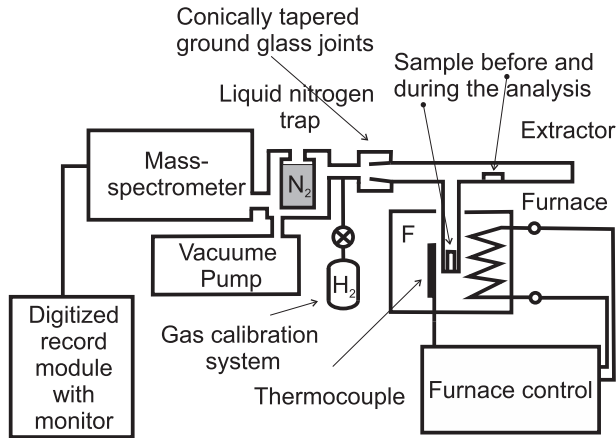Fig. 1 — Hydrogen analyzer AV-1 (a) and its extraction system (b).

Fig. 2 — **Scheme of the hydrogen measurement in AV-1.**

The schematic picture of the sample is shown in Fig. 3. The prismatic sample sizes are: $a = 2.5$ mm; $l = 2$ mm; $b = 2$ mm.

The extractor walls are made of fused silica. In the process of analysis, their temperature is maintained at a constant value T_0. The fused silica has practically zeroth thermal conductivity, the area of the sample contact with the walls is small, so that the heat transfer occurs only due to radiation.

The fused silica does not transmit infra-red radiation of the radiation furnace 4, so that the sample is heated due to the heat radiation of the extractor walls. The amount of heat absorbed by the sample during the interval dt is:

$$dQ = \varepsilon_n \sigma S (T_0^4 - T^4) dt, \tag{1}$$

where $\sigma = 5,6687 \cdot 10^{-8}$ W/m^{2}K^4- Stephan Boltzmann constant, T — the sample temperature, T_0 — the temperature of walls of the analytical (see Fig. 1) of extractor, ε_n is the absorption coefficient of the studied sample.

$$\varepsilon_n = \frac{1}{\frac{1}{\varepsilon_t} + \frac{S}{S_2}\left(\frac{1}{\varepsilon_2} - 1\right)},$$

ε_t is the absorption coefficient of titanium, ε_2 is the absorption coefficient of walls of fused silica of analytical appendix of extractor (equal to 1 for infrared radiation), S is the sample area, S_2 is the area of wall of analytical appendix of extractor involved in the heat transfer.
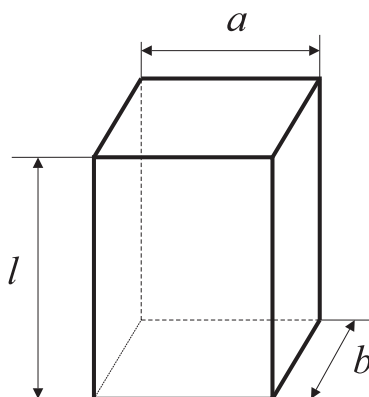

Fig. 3 — **The analyzed sample.**

If $\varepsilon_2 = 1$ or is much higher than ε_t then the approximate relation $\varepsilon_n \approx \varepsilon_t$ can be used. In the range of temperatures of interest, 200 °C—900 °C, for titanium this yields.

$$\varepsilon_t = 0.2. \tag{2}$$

In this condition, the heat capacity of titanium weakly depends on temperature and equals $c = 0.6$ kJ/kg K. The heat dQ (1) absorbed by the sample gives rise to the increase in its temperature by dT:

$$dQ = c\rho V dT, \tag{3}$$

where ρ is the density, V is the volume of the sample.

From equations (1)–(3) one obtains the following equation for the sample heating:

$$\frac{dT}{dt} = \frac{\sigma S}{c\rho V} \cdot 0.2 \cdot (T_0^4 - T^4). \tag{4}$$

Dependence of hydrogen concentration in the sample on the coordinates and time is obtained from solution of the time-dependent diffusion equation.

$$\begin{aligned} \Delta C &= \frac{1}{D}\frac{\partial C}{\partial t} \\ C|_s &= 0 \\ C|_{t=0} &= C_0 \end{aligned}, \tag{5}$$

where C is the hydrogen concentration in the sample, $D = D_0 \cdot \exp(-u/kT)$ is the diffusion coefficient for hydrogen in metal, u is the hydrogen activation energy, D_0 is the diffusion constant, k is the Boltzmann constant.

In the given boundary conditions, the first term of the Fourier expansion for the hydrogen concentration C of the solution of Eq. (5) can be written as.

$$C(x,y,z,t) = \frac{C_0\pi^3}{8}\sin\frac{\pi x}{a}\cdot\sin\frac{\pi y}{b}\cdot\sin\frac{\pi z}{l}\cdot f_1(t,u,D_0) \tag{6}$$

where l, a, b are the height and transversal sizes of the sample, respectively. The function $f_1(t,u,D_0)$ is a solution of the equation.

$$f_1 + D_0\cdot\exp\left(-\frac{u}{kT}\right)\left(\frac{\pi^2}{a^2} + \frac{\pi^2}{b^2} + \frac{\pi^2}{l^2}\right)f_1 = 0, \ \ f_1(0,u,D_0) = 1. \tag{7}$$

In experimental analysis of the sample, the apparatus registers time evolution of the total hydrogen flux $q(t)$ thought the area of the sample. According to the low of Fick we have:

$$q(t) = -\int_S D\frac{dC}{dn}dS, \tag{8}$$

where S — sample surface.

Integration of (8) with the use of the equation (6) for the hydrogen concentration C yields:

$$q(t) = \pi^2 C_0 abl \cdot \left[\frac{1}{a^2} + \frac{1}{b^2} + \frac{1}{l^2}\right]\cdot D_0\cdot\exp\left(-\frac{u}{kT}\right)\cdot f_1(t,u,D_0). \tag{9}$$

When assuming that hydrogen in the sample is contained in the reversible traps with different binding energies u_i and the corresponding diffusion constants D_{0i} and initial hydrogen concentrations C_{0i} one can use the superposition principle, because of linearity of the diffusion equation (5).

In this case time dependence of the hydrogen flux from the sample $q(t)$ will be defined by the following sum:

$$q(t) = \pi^2 abl \cdot \left[\frac{1}{a^2} + \frac{1}{b^2} + \frac{1}{l^2}\right] \cdot \sum_i C_{0i} \cdot D_{0i} \cdot \exp\left(-\frac{u_i}{kT}\right) \cdot f_1(t, u_i, D_{0i}), \tag{10}$$

where $f_1(t, u_i, D_{0i})$ is a solution of the equation (7) at the given values of the constants u_i, D_{0i}, C_{0i} and the sample geometry (l, a, b).

Comparison between the experimental extraction curve and the calculated curve (10) at the chosen values of initial concentrations C_{0i} and diffusion constants u_i and D_{0i} yields the values of activation energy and diffusion constants for hydrogen in metal.

Fig. 4 shows the plots of extraction curves measured experimentally and obtained by model calculation using the equation (10).

Therefor the extraction curve measured by the hydrogen analyzer AV-1 using the vacuum heating method one to determine fundamental parameters characterizing the state of hydrogen in the solid, the energy levels of hydrogen u_i, the concentration of hydrogen C_{0i} in different energy states (populations of energy levels), the diffusion constant D_{0i} for hydrogen with binding energy u_i.

Verification of main approximations of method for determination of binding energies

For experimental testing of reliability of the accepted assumption, the samples of titanium alloy PT7M were prepared which had shape of parallelepiped with the sizes 2*2*2.5 mm. The samples were cut from a tube with the outer diameter of 28 mm.

Six samples with the same sizes were loaded in the extraction system of the hydrogen analyzer AV-1. Testing of each sample was performed at a fixed extraction temperature, beginning with 550 °C and ending by 800 °C. In each test the analytical appendix of the extraction system was heated up to the extraction temperature without the sample, then the sample was placed to the heated analytical appendix, and the extraction curve was measured. Each sample was tested one time, i.e. at low temperature only a part of hydrogen was extracted from the sample. The results of these tests are shown in Fig. 5.
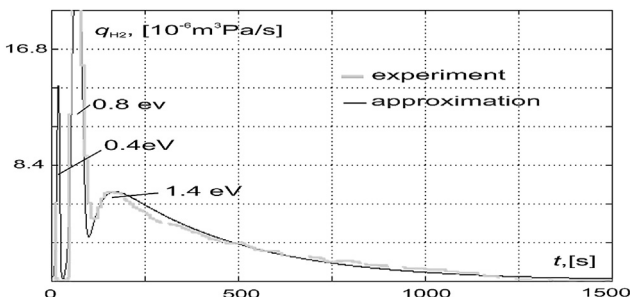

Fig. 4 − Experimental and calculated extraction curves with three maxima for the titanium alloy PT7M.
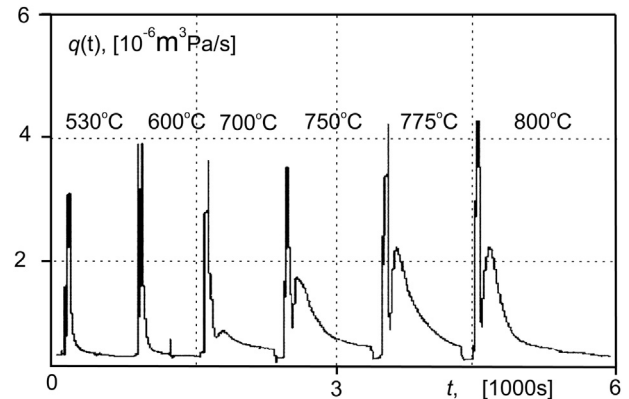

Fig. 5 − Experimental extraction curves for samples of the titanium alloy PT7M obtained at different extraction temperatures (indicated above).

Analysis of the extraction curves shows that the hydrogen diffusion from titanium alloy has an activation character. Hydrogen having higher binding energy remains in the sample after performing the analysis for the extraction temperatures less than 700 °C.

If the assumption about existence of states with different binding energies u_i and corresponding diffusion constants D_{0i} is valid then it is possible to describe adequately the measured extraction curves for other temperatures.

Modeling of the process of high-temperature vacuum extraction was performed six times at different extraction temperatures, with calculation of flux of extracted hydrogen using the equation (10).

The modeling result is shown in Fig. 6. All the calculated extraction curves, obtained at the analysis temperatures of 530 °C, 600 °C, 700 °C, 750 °C, 775 °C, 800 °C, are given on one plot, in analogy with the experimental curves presented in Fig. 5.

The obtained results of the modeling show good agreement with experiment. In this modeling, were used the parameters of diffusion that determined by analysis of the experimental extraction curve obtained at the analysis temperature of 800 °C. It became possible, without using adjustable parameters, to make extrapolation to lower temperatures and obtain result adequate to the corresponding experiment.

Thus the proposed model is adequate to the real physical process occurring in realization of the method of high-temperature vacuum extraction of hydrogen from analyzed sample of solid probe.

In the model describing the process of the sample heating, only transfer of heat due to radiation was taken into account. Possible sources of uncertainly in determination of activation energy of diffusion are as follows:

(i) non-zeroth thermal conductivity of fused silica,
(ii) uncertainty in the used value of the coefficient of absorption of heat radiation.

The following experiment was performed to test the proposed model of the sample heating.
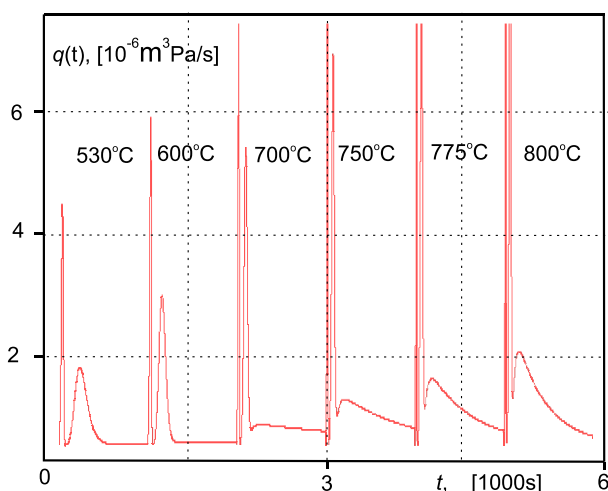
Fig. 6 – **Results of modeling of extraction curves for the titanium sample PT7M at different extraction temperatures (indicated above).**

Two samples with the sizes: diameter $2a = 8$ mm, length $l = 15$ mm were machined from the same rod of the aluminum alloy AMg6. Before loading in the extractor one of the samples was covered with soot obtained in incomplete combustion of acetylene.

The sample heating was minimal due to small time of contact between the sample and the flame of burner containing soot.

The working temperature of the extraction system 530 °C was set. The blackened sample was placed in the analytical appendix using a magnetic pusher without spoiling vacuum.

The extractor wall temperature is maintained equal to the working temperature of analysis. The cold sample (at room temperature) is heated up to the extraction temperature and then it is heated at this temperature up to the end of analysis.

A standard sample has small absorption ability natural for the aluminum alloy. Meanwhile the sample covered with soot has an absorption ability practically equal to 1.

The extraction curves for blackened and standard samples were measured. They are shown in Figs. 7 and 8. It is established that the sample covered with soot was heated about 20 times faster. If one suppose that the hydrogen diffusion has activating character then the extractor curve can provide information on velocity of sample heating.

The first peak on the extraction curve is associated with absorption of "surface" hydrogen from the sample. The maximum position corresponds to the sample temperature 100–150 °C.

In modeling dynamics of sample heating the equation (4) was used. For the sample covered with soot the absorption coefficient was accepted to unity. Fig. 9 shows results of modeling of dependence of the sample temperature on time.

The curve 1 corresponds to the sample covered with soot. The curve 3 is obtained for pure polished aluminum, and the

curve 2 corresponds to the sample of aluminum alloy AMg6 prepared in accordance with requirements of [19]. The absorption coefficient of the sample corresponds to the experimental curve presented in Fig. 8.

Analysis of the presented results of modeling dynamics of the sample heating allow as to make conclusion that the real absorption coefficient for aluminum alloys is higher than that for pure polished aluminum presented in literature. Probably this is caused by existence of alloying and quality of treatment of the sample surface. The performed experiments show that the real absorption coefficient can be determined for each kind of alloy.

The above technology of comparative analysis of amount of hydrogen in the samples with regulated absorption coefficient allows more precise determining temporal dependence of the sample temperature during the process of analysis.

Other methods for determination of sample temperature in vacuum either distort considerably results of the analysis or have low accuracy.

Fastening of a thermocouple on the sample in vacuum makes experiment and extraction system very cumbersome. At $T = 500–600$ °C it is necessary to isolate the thermocouple conductors by special materials: the insulators themselves and thermocouple materials can contain hydrogen, that will give rise to essential distortion of result of the analysis, especially in determination of small concentrations of hydrogen. Fastening the thermocouple is possible only by its pressing in a cavity or in the orifice of the sample, that result in considerable plastic deformation of material, even at the sample masses of about 2–5 g.

Mounting of the thermocouple on a special pedestal or melting pot leads to the fact that material of the pedestal itself or melting pot can distort considerably results of the analysis. The use of pyrometers for determinations of the sample temperature does not provide the necessary accuracy in conditions of large hitch created by heat radiation of the furnace. Moreover, at $T < 500$ °C the pyrometry has uncertainty higher than ± 50 °C.

Therefore the proposed experimental procedure for determining time dependence of the sample temperature in realization of the method of high temperature vacuum-extraction of hydrogen allows one to obtain reliable data on the value of absorption ability of the sample surface and to get adequate results in approximation of the extraction curves for determination of binding energies u_i and the diffusion constants D_{0i} for hydrogen in various materials.

Discussion of results

In determination of binding energy by the method of thermo-desorption spectra, no assumption about parameters of samples is used. The algorithm for determining the binding energies seems independent and objective. Such independence is not always supported by experiment. In Ref. [14] the shape and sizes of samples were taken into account, that changed essentially the data on binding energies. The study [20] of steels of one particular type showed large spread of values of diffusion parameters, and, apart from that, the values of the activation energy u_i and the diffusion constant
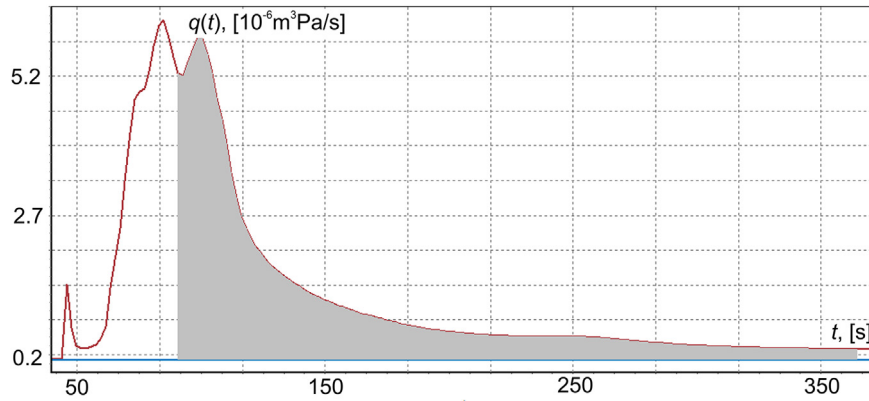
Fig. 7 − Initial part of the extraction curve obtained for the sample of aluminum alloy AMg6 covered with soot.

D_{0i} were strongly depended of sizes of the studies samples (as observed also in Ref. [14]).

The TDS method is based on the trap hypothesis which states that there exists only one channel for hydrogen diffusion in a solid and traps are uniformly distributed in the sample. Hydrogen is accumulated in the traps. Physical considerations that diffusion is only model for the process of statistically equilibrium variation of states of atoms and molecules are not taken into account. The equations for hydrogen diffusion and amount of hydrogen in traps are different. Consider the contradictious arising in such approach in the case of thin samples.

Let us consider that hydrogen can be contained in traps of several types (with different binding energies or activation energies). After escaping from the traps hydrogen passes to a diffusion-mobile state with binding energy u_0. In this state hydrogen diffusion is possible in a thin layer of the thickness l in direction of the Ox axis. The cross section of the layer is shown in Fig. 10.

The equation for deallocation of hydrogen from traps with binding energy u_i has a standard form:

$$\frac{dw_i}{dt} = -D_i w_i$$
$$w_i(0) = w_{i0}$$

(11)

where $w_i(t)$- is the concentration of hydrogen in the trap reduced to the mass of alloy.

$D_i = D_{0i} e^{-u_i/kT(t)}$- is the coefficient of speed of trap deallocation, D_{0i} is the trap deallocation constant analogous to the diffusion constant, k is the Boltzmann constant, $T(t)$ is the layer's temperature (dependent of time). Let us assume that the distribution of traps over the layer's volume is not uniform, $w_i(t,x) = w_i(t)sin(\pi x/l)$

It follows from the equation (11):

$$w_i(t) = w_{i0} \exp\left(-\int_0^t D_i(\theta)d\theta \right).$$

The diffusion equation is written as.

$$\frac{\partial w}{\partial t} = D\frac{d^2 w}{dx^2} - \sum_i \frac{dw_i}{dt},$$
$$w(t,0) = w(t,l) = 0$$
$$w(0,x) = w_0 \sin\left(\frac{\pi x}{l}\right)$$

(12)

Here $D = D_0 e^{-u_0/kT(t)}$ — is the diffusion coefficient, w is mass concentration of hydrogen in the layer, the source terms describing the flux of hydrogen from traps inside the layer. Using (11) we can rewrite the diffusion equation in the form:
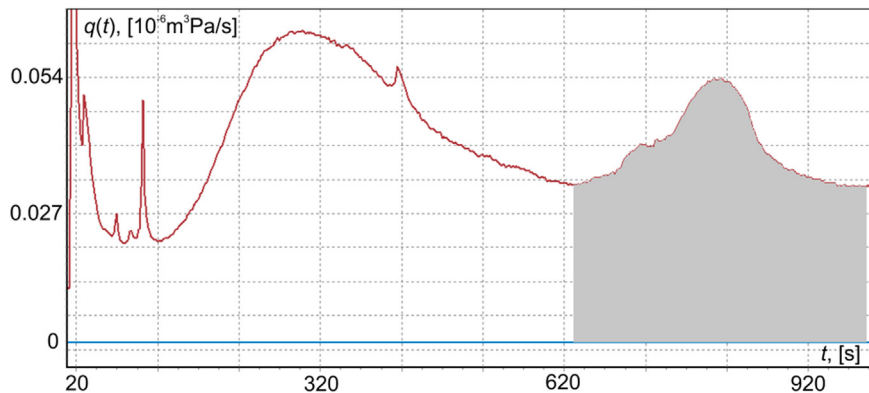

Fig. 8 − Initial part of the extraction curve obtained for the sample of aluminum alloy AMg6. The sample area is without blacking.
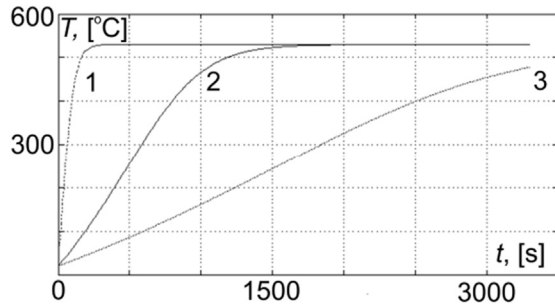
Fig. 9 − Dependence of temperature of analyzed sample on time. Modeling is performed at different values of absorption coefficient: the curve 1 corresponds to the sample is covered with soot $\varepsilon_t = 1$; the curve 2 corresponds to the sample is prepared according to [19] $\varepsilon_t = 2\cdot10^{-4}\cdot(T + 64,3)$; the curve 3 is obtained for pure polished aluminum $\varepsilon_t = 7\cdot10^{-5}\cdot(T + 64,3)$.

$$\frac{\partial w}{\partial t} = D\frac{d^2 w}{dx^2} + \sum_i D_i w_i, \tag{13}$$

$$w_t(t) = w_0\exp\left(-\frac{\pi^2}{l^2}\int_0^t D(\theta)d\theta\right) + \int_0^{\int_0^t D(\theta)d\theta} \exp\left(-\frac{\pi^2\left(\int_0^t D(\theta)d\theta - \theta\right)}{l^2}\right) \times \sum_j\left[\frac{D_j(\theta)}{D(\theta)}w_{j0}\exp\left(-\int_0^\theta D_i(\sigma)d\sigma\right)\right]d\theta \tag{17}$$

The substitution $\tau = \int D(t)dt$ yields.

$$\frac{\partial w}{\partial \tau} = \frac{d^2 w}{dx^2} + \sum_i \frac{D_i}{D}w_i,$$
$$w(\tau, 0) = w(\tau, l) = 0 \tag{14}$$
$$w(0, x) = w_0\sin\left(\frac{\pi x}{l}\right)$$

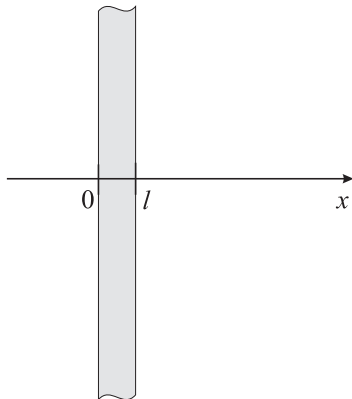General solution of the uniform problem is written as.

Fig. 10 − Schematic picture of the cross section of the thin layer.

$$w(\tau, x) = w_0\sin\left(\frac{\pi x}{l}\right)\exp\left(-\frac{\pi^2}{l^2}\tau\right), \tag{15}$$

Solution of non-uniform problem is written as.

$$w(t, x) = w_0\exp\left(-\frac{\pi^2}{l^2}\tau(t)\right)\cdot\sin\left(\frac{\pi x}{l}\right) + \int_0^{\tau(t)}\exp\left(-\frac{\pi^2(\tau(t) - \theta)}{l^2}\right)$$
$$\times \sum_j\frac{D_j(\theta)}{D(\theta)}w_j(\theta)d\theta\cdot\sin\left(\frac{\pi x}{l}\right) \tag{16}$$

The first important conclusion is that the ratios $D_j(\theta)/D(\theta) = D_{0j}/D_0\exp(-u_j-u_0/kT(\theta))$ are involved in the convolution of (16), so that it is possible to consider hydrogen ready to diffusion as molecules located in a trap with binding energy u_0, and liberation of hydrogen from traps as a transition from the level with energy u_j to the level with energy u_0 occurring with the energy loss (u_j-u_0).

Now let us rewrite the time-depended factor in (16) accounted for time substitution and solutions for mass concentrations w_j:

and consider the case of very thin layer. Then equation (11) can be written as:

$$w_t(t) \approx w_0\exp\left(-\frac{\pi^2}{l^2}\int_0^t D(\theta)d\theta\right)$$
$$+ \frac{l^2}{\pi^2}\sum_j\left[\frac{D_j\left(\int_0^t D(\theta)d\theta\right)}{D\left(\int_0^t D(\theta)d\theta\right)}w_{j0}\exp\left(-\int_0^{\int_0^t D(\theta)d\theta} D_i(\sigma)d\sigma\right)\right] \tag{18}$$

There is a principal difference between exponents of the first and second components of the sum (18), namely. In the former case, exponent is multiplied by the scaling factor π^2/l^2, but in the later case this is not. Consequently, diffusion from traps practically does not depend on the thickness of a layer, in contradiction to the experimental data.

In experiments with films of 7−10μm thick, the duration of hydrogen peaks on the extraction curve amounts 7−10 min.

Attempts for modeling fluxes of "natural" hydrogen from samples with thickness of 10 μm using the model of "one-channel" diffusion lead to the fact that the activation energy

Table 1 – The activation energies of the hydrogen determined for titanium alloys using different models: a multi-channel diffusion (PT7M alloy) and the classical TDS method [13].

PT7M ($\alpha + \beta$ alloy) eV	Ti–6Al–4V ($\alpha + \beta$ alloy) [21] eV	β −21S (β alloy) [22] eV	β −21S (β alloy) [23] eV	Ti−6.8Mo−4.5Fe−1.5Al (β alloy) [24] eV
0.4	(1.04−1.29)[a,b]	0.12	1.15[a,c]	(0.49−0.66)[a,d]
0.8		0.280		
1.4		1.06		

[a] Only one pick TDS was observed.
[b] Depends on the method of the hydrogen introducing into the alloy.
[c] After hydrogen introduced by GTAW welding in a mixed Ar + 5% H_2 shield.
[d] Depends on the hydrogen saturation time.

of the diffusion channel itself has reasonable values, 0.2−0.4 eV, and binding energies in traps yield additional several hundredths eV. Thus energy of thermal motion at room temperature is sufficient for effective emptying of traps.

On the contrary the multichannel model yields the difference between activation energies of different channels in the range 0.4−1.0 eV.

Therefore the experimental data, physical arguments and relevant mathematical modeling show that the multichannel model of hydrogen diffusion gives more accurate description of experimental results.

There is one additional source of errors of the TDS method. It consists in existence of background fluxes of hydrogen from the extraction system, which depend on the sample's temperature. The temperature of surrounding parts of the extraction system increases with the heating of the sample. In some cases the background flux of hydrogen increases by several hundred times in the course of measurement of TDS [9].

Table 1 shows the comparison the activation energies for different channels of the hydrogen diffusion in the titanium alloy PT7M and the hydrogen desorption activation energies obtained by the TDS.

Preliminary saturation of samples with hydrogen widely used in the TDS method allows one to reduce the influence of background fluxes. To estimate their influence in measuring natural concentrations of hydrogen, an experiment was performed on stepwise changing temperature of the extraction system of the hydrogen analyzer AV-1. Fig. 11 shows the extraction curve for the aluminum alloy sample with the mass of 2 g and hydrogen concentration 0.2 ppm (gray peak), and background fluxes arising in the stepwise heating of the extraction system up to 700 °C (left).

The hydrogen flux from the walls of extraction system is the same as that from the studied sample (as seen from Fig. 11). Thus, the heating of the extraction system during TDS can be a source of error in determining of hydrogen bonding energy.

Prehydrogenated samples typically applied when TDS is used. During preliminary saturation, we obtain a new hydrogen-material system whose properties may be differ
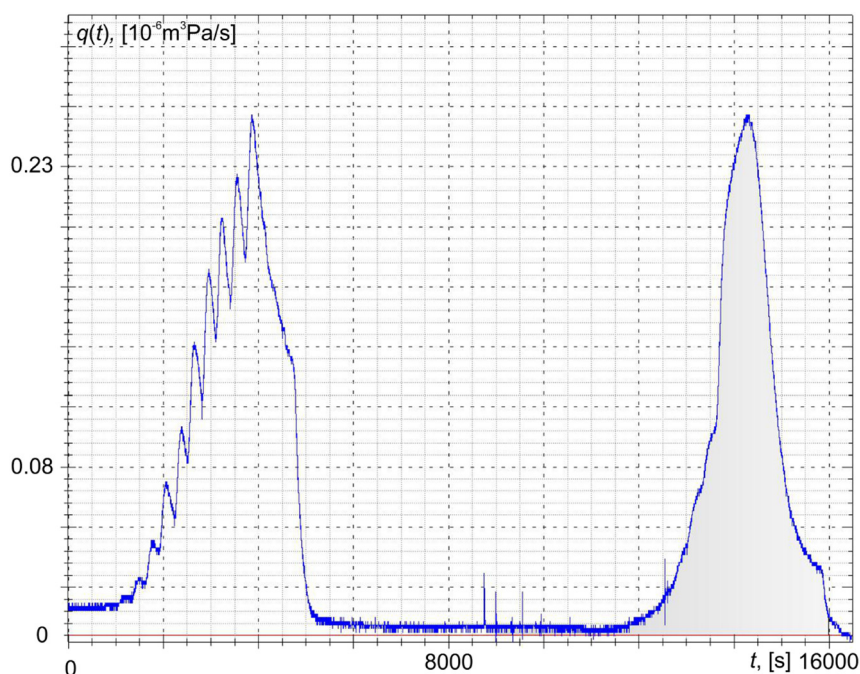

Fig. 11 – The extraction curve for the background fluxes arising in the stepwise heating of the extraction system up to 700 °C (left) and the aluminum alloy with the mass of 2 g and hydrogen concentration 0.2 ppm (gray peak).

from those of the original material (see Table 1). As is well known, increasing of hydrogen concentration leads to changing of the material's properties. For example: casting of aluminum alloys are cracked in the process of crystallization if in the event that hydrogen concentration is just twice the normal one. As it was shown in Ref. [25] for steels, the saturation of material with hydrogen gives rise to decreasing tensile strength to the 3—5 times. So strong point of our method is opportunity to measure binding energy of hydrogen without special hydrogenation of samples.

Conclusions

This study shows that by using the experimental technique high temperature vacuum extraction the model of multi-channel diffusion gives a more precise description of the real hydrogen diffusion in solids of than other approaches.

Application of the method of high temperature vacuum extraction with mass-spectrometric measuring instant values of the hydrogen fluxes allows measuring small natural hydrogen concentrations and distribution of these concentrations over activation energy.

There is no need on preliminary saturation of the samples by hydrogen in experiments. High sensitivity of analysis using AV-1 makes it possible to trace evolution of natural hydrogen in the sample under different thermo-mechanical and physical-chemical effects.

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