**Beckman I.N.**

# A FULL-SCALE STUDY OF GAS DIFFUSION IN VACUUM EQUIPMENT MATERIALS. 3. THE PHENOMENOLOG1CAL THEORY ON HYDROGEN PERMIABILITY UNDER THE PRESENCE OF PURIFICATION OR CONTAMINATION PROCESSES ON MEMBRANE SURFACES

## 1. Introduction

It is known that molecular hydrogen undergoes reversible chemical reaction of dissociatio-association [1, 2]. Moreover, since hydrogen is a chemically active element, then in the course of diffusion through metal foils it reacts with a solid matrix which results in hydrides formation. Besides, hydrogen reacts with impurities and that leads to volatile or unvolatile products formation. Due to compound chemical reactions with hydrogen taking part in them, the kinetic curve shapes of permeability considerably change, there appear breakups, minima and maxima in the graphs of the diffusion coefficient temperature dependence, or diffusion constants plotted in Arrenius coordinates, the effective diffusion coefficient becomes dependent upon the membrane thickness and partial hydrogen pressure at penetration into the membrane. On the other hand, the chemical reactions can be usefully applied to control the vacuum equipment degassing.

The present work is aimed at studying a diffusion mathematical model characterised by different chemical reactions with the materials studied. The reactions in their turn result in either purification or contamination of membrane surfaces when hydrogen permeates through them. The main attention is given to phenomenological theory consequences analysis of active gases and evaluation methods of hydrogen interaction with impurities occuring either on the surface or near-surface membrane layers; these methods are based upon the diffusion data obtained with the help of permeation method.

## 2. Chemical reaction of the phase boundaries occurring when hydrogen permeats through metal membranes

When hydrogen permeats through a pure metal which can't react with hydrogen the dominant reaction taking place on membrane surface is the reversible dissociation-association reaction:

$$H_2 \underset{k_2}{\overset{k_1}{\rightleftarrows}} 2H \qquad (1)$$

In this case, the dissociation is described by formal kinetics of the first order chemical reaction while the re-combination is described by the kinetics of the $2^d$ order reaction. This fact leads to some non-linear boundary conditions of the $3^d$ kind. The process of hydrogen transition from a gas phase into a solid one consists of several consequent steps: molecular hydrogen adsorption, dissociation-recombination reaction, atomic hydrogen adsorption and ionised hydrogen transition in the solid volume (at this moment an additional potential barrier is created due to the different properties of the near-surface layers and bulk materials). On the membrane exit side, such processes have reverse order. As the permeation method uses different hydrogen partial pressure affecting both the entrance and exit sides of membrane, the degassing and solution processes under the conditions of a certain experiment may include different number of the limiting stages. Here, it should be stressed that conditions determining the parameters of the same stage both at the entrance and exit membrane sides have different values. In general, hydrogen permeation processes description according to the reaction (1) requires the diffusion equation solutions under generalised non-linear and non-stationary conditions of the $3^d$ kind [2].

The situation becomes much more complicated when membrane surfaces and materials contain impurities. Since the surface contains inhomogeneous elements the notion of adsorption and catalytic centers of the reaction (1), and consequently the notion of the adhesion coefficient spectra and other parameters describing diffusate atom exchange rate between different sites where hydrogen is captured, should be introduced into the for kinetics of hydrogen permeation. The impurities may considerably change the velocity of practically all the stages of hydrogen solution-degassing in a metal. For example, when nickel contains palladium inpurities the atomic hydrogen formation dominates in the reaction (1) - the so-called "spillover" effect, while sulphur impurities (catalytic poison) are able to block the reaction (1) completely, and consequently stop hydrogen permeation through a nickel membrane. Some of surface impurities possess a trap action, i.e. hydrogen quatity increases on metal surface while the hydrogen flow permeated through a membrane decreases. Besides, membrane surface impurities are able to form poly-layers which not only greatly change the number and types of adsortion and catalytically active centers, but result in additional resistance to diffusion (in some cases a diffusion model for multi-layer media should be used for hydrogen permeation description).

The most important circumstance is the possibility to change the structure and composition of membrane near-surface layers during the process of hydrogen permeation. Indeed, at high temperatures hydrogen reacts with impurities what is followed by gaseous and solid products formation, e.g. according to the equation:

$$H_2 + R \Leftrightarrow 2HR, \qquad (2)$$

where R is one of the elements (0, C, S etc).

For example, the following reactions of common impurities with hydrogen may occur in nickel:

$$H_2 + \begin{cases} O \to H_2O \\ C \to CH_4 \\ C \to C_2H_4 \\ C \to C_2H_2 \\ S \to H_2S \end{cases}$$

and some others. Either all the reaction take place or one of the reactions is dominant - everything depends on impurity composition, temperature and hydrogen pressure. It is evident that intensive hydrogen reaction with impurities excludes molecular hydrogen flow at the membrane exit, no matter how large the diffusion coefficient and membrane thickness are.

Compound chemical reactions with impurities on metal surface lead to the following:

1) The reactions exclude hydrogen from the diffusion process, decrease the flow at the membrane exit and delays the diffusion stationary state establishment.

2) In the course of chemical reactions with surface impurities the surface is either purified (the number of centers available hydrogen adsorption increases) or contaminates (non-volatile products are deposited on the membrane surface).

3) As a result of hydrogen reaction with impurity polylayers these layers are etched. It is noteworthy, that hydrogen does not penetrate the sample until the process finishes. The polylayer reactions at the membrane exit delay the degassing. Only after discontinuities appear in the impurity layer, hydrogen permeation process starts to develop. In this case, the time required for the stationary state establishment is prolonged. One can be aware of the fact that non-stationary conditions do not exist anymore only after all the reactions on both the entrance and exit sides of the membrane have stopped.

4) Due to the considerable differences in the reaction activation energies (with hydrogen taking part in them) some new reactions are involved into the chemical processes as the temperature increases while the old ones disappear, since one of the reaction components is lost (impurity element). Therefore, chemical reactions are expected to affect hydrogen permeation kinetic curve shapes to great extent.

Different hydrogen reactions with impurities (e.g. interaction with oxygen resulting in the near-surface oxide reduction) leading to gaseous or low-volatile products formation may take place in the bulk of the metal. The reaction products diffusing in the bulk of metal take part new multi-staged chemical reactions with hydrogen.

It should be stressed that element composition of the surface and the bulk of the material may change in the course of the diffusion experiment and it is not only due to the chemical reactions with hydrogen. Space-time composition alterations occur during phase transitions in a metal (polymorphic transformations, transitions of the order-disorder type, etc) or they appear as a result of an external influence upon the sample which modifies the material structure.

There's no doubt that phase-boundary processes produce considerable effect upon hydrogen permeation kinetics and degassing of metals, and of cause they must be taken into account for design of materials and vacuum equipment.

## 3. The generalized non-stationary non-linear boundary conditions of the third kind used in the description of hydrogen permeation through a membrane with inhomogeneous element composition of the surface

Let us assume that a membrane exit surface contains n-types of adsorption or catalytically active centers (e.g., nickel, the surface of which has the following composition: nickel, carbon and sulphur, i.e. n = 3). The surface part which is filled with 1th center types is equal to $N_{i,a}$ $\left(\sum_{i=1}^{n} N_{i,a} = 1\right)$. Suppose that each type of the impurities involves the following processes: molecular hydrogen adsorption, the dissociation-recombination reaction (1), molecular hydrogen adsorption and hydrogen transition through the near-surface layer with specific properties into the bulk of the metal (3). Further on, we assume that undisturbed interstitial hydrogen diffusion takes place in the bulk of the membrane. Then, to describe the hydrogen permeation kinetics through membrane one must solve the diffusion equation:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \qquad (3)$$

under the boundary conditions at the membrane exit:

$$N_{i,a}\frac{d\theta_i}{dt} = k_{i,1\infty}p_0(1-\theta_i-\vartheta_i) - k_{i,1\infty}\theta_i - k_{i,12}\theta_i(1-\theta_i-\vartheta_i) + k_{i,21}\vartheta_i^2 \qquad (4a)$$

$$N_{i,a}\frac{d\vartheta_1}{dt} = 2k_{i,12}\theta_i(1-\theta_i-\vartheta_i) - 2k_{i,21}\vartheta^2 + (1-\theta_i-\vartheta_i) - k_{i,23}\vartheta_i(1-\omega_i) \qquad (4b)$$

$$N_{i,c}\frac{d\omega_i}{dt} = -k_{i,32}(1-\theta_i-\vartheta_i)\omega_i + k_{i,23}\vartheta_i(1-\omega_i) - k_{i,34}\omega_i(1-\chi_{ia}) + k_{i,43}(1-\omega_i)\chi_{i,0} \qquad (4c)$$

$$\pm J\Big|_{x=0} = C_{m,i}D\frac{\partial\chi}{\partial x}\Big|_{x=0} = k_{34}\omega_i(1-\chi_{10}) - k_{43}(1-\omega_0) \qquad (4d)$$

A similar set of equations could be written for the membrane exit surface.

Here, $\theta = \frac{C_{H2,a}}{N_{a,H2}}$; $\vartheta = \frac{C_{H,a}}{N_{a,H}}$; $\omega = \frac{C_{H+,S}}{N_S}$; $\chi = \frac{C_{H+,v}}{N_v}$

$N_{H2,a}$ is the concentration of centers for hydrogen atoms and molecules adsorption on the membrane surface, correspondingly. $N_S$ is the concentration of the sites assessible for hydrogen acceptance in the first boundary layer of vacancies, $N_v$ - vacancy concentration in the bulk of the metal assessible for hydrogen solution, $C_{H2}$ and $C_H$ - hydrogen and molecule concentrations adsorbed in the membrane surface, $C_H$+,s, $C_H$+$_{,v}$ - hydrogen atom concentration diluted in the first near-surface layer of vacancies and in the bulk vacancies (θ and v - the extent of the surface filling with hydrogen atoms and molecules, ω and χ - the extent of filling the surface layer and bulk vacancies), $C_M$ - maximum hydrogen concentration in the bulk of the metal, $N_m$ - the number of sites assessible for hydrogen solution (if one site is able to accept one hydrogen atom, then $N_m = C_m$).

If there is a local balance, then the non-stationary boundary conditions (4) transform into the stationary ones. Therefore, the solution and diffusion processes are controlled by the equilibrium constants of the corresponding reactions

$$K_{H2,a} = \frac{k_{\infty 1}}{k_{1\infty}};\ K_{H,a} = \frac{k_{12}}{k_{21}};\ K_S = \frac{k_{23}}{k_{32}};\ K_v = \frac{k_{34}}{k_D}$$

where $K_D$ is the diffusion velocity constant, $K_D=D/d^2$, d -the lattice constant, D - hydrogen diffusion coefficient (in the form of a proton) over the bulk of the metal.

The temperature dependence of chemical reaction kinetic constants on the surface may be described by the following expression:

$$K_i = K_{io}\exp(E_i/RT), \qquad (5)$$

where activation energy $E_i$ could have either positive or negative value.

The diffusion coefficient temperature dependence has the following form:

$$D = D_0\exp(-E_D/RT) \qquad (6)$$

If the concentration of adsorption, catalytic and absorption centers doesn't depend on the temperature, then the change of the contribution by a certain impurity type in the total transmembrane transport process is determined by the first exponential factor values and by the velocity constant activation energies of the corresponding chemical reactions and the diffusion coefficient.

The impunity diffusion in a metal or out of it results in the change of adsorption centers concentration according to the exponential law (either increasing or decreasing). The presence of phase transitions (of the first or second kind), order - disorder type transitions may expel the impurity out, or it may be fully "drown" in the metal (it depends on the lattice parameter changes during the transition and upon the impurity atom diameters). As a result, the $N_a(T)$ independence has S-form or a peak shape. Such alteration of element composition of the surface or near-surface layer may result in the cardinal change of hydrogen permeation kinetics. To sum it up, the importance of membrane surface element composition control is of vital importance for correct experiments on gas diffusion in solids,

## 4. The effect of membrane surface element composition change upon permeation kinetics

As mentioned above, hydrogen being a chemically active element may react with surface impurities during the diffusion process affecting the surface element composition. When hydrogen is out of the diffusion process the permeability kinetic curve shape may be considerably distorted. Let us study the model of hydrogen permeation kinetics through a metal membrane. In this case, the membrane surface contains the impurity which is able to react with hydrogen. We assume that reversible chemical reaction is defined by the expression (2). It should be stressed here that the reaction product could be either highly volatile and it is removed out of the membrane surface which result in the surface purification, or it may be non-volatile which leads to a higher degree of the surface contamination.

Let F(t) describe the hydrogen concentration change with the time (the hydrogen involved into the permeation process). This change occurs as a result of the chemical reaction which takes place at the membrane exit or entrance:

$$F(t) = \frac{C_S - C_{S,\infty}}{C_{S,0} - C_{S,\infty}} \qquad (7)$$

where $C_S(t)$ is the current hydrogen dynamic concentration in the near-surface membrane layer at the time moment t, while $C_S$,0 is the initial hydrogen concentration at the time moment t=0, and $C_S$,∞ is the hydrogen concentration on mem-brane surface when a stationary hydrogen flow through a membrane is established, i.e. after all the purification (contamination) processes on the membrane surface have stopped and after the completion of all the non-stationary diffusion processes in the bulk of the metal. It should be stressed thatbfrom the physical point of view F(t) function for the entrance side of membrane has been defined at the beginning of the experiment, while for the exit side it is defined when hydrogen reaches the exit side of the sample.

Since the membrane surface hydrogen concentration is assumed to depend upon the amount of impurities contained on the surface, then F(t) function could be considered as changing function during the hydrogen permeation process. To characterise the degree of surface purity quantitavely the parameter

$$\alpha = \frac{C_{S,\infty} - C_{S,0}}{C_{S,\infty}} \qquad (8)$$

should be introduced. If the membrane surface is purified during the hydrogen permeation process, then $C_{S,\infty} > C_{S,0}$ and $\alpha > 0$ $(0 \le \alpha \le 1)$. If contamination takes place, then $Cs,\infty < C_{S,0}$ and α<

0 ($-1\le\alpha\le 0$).

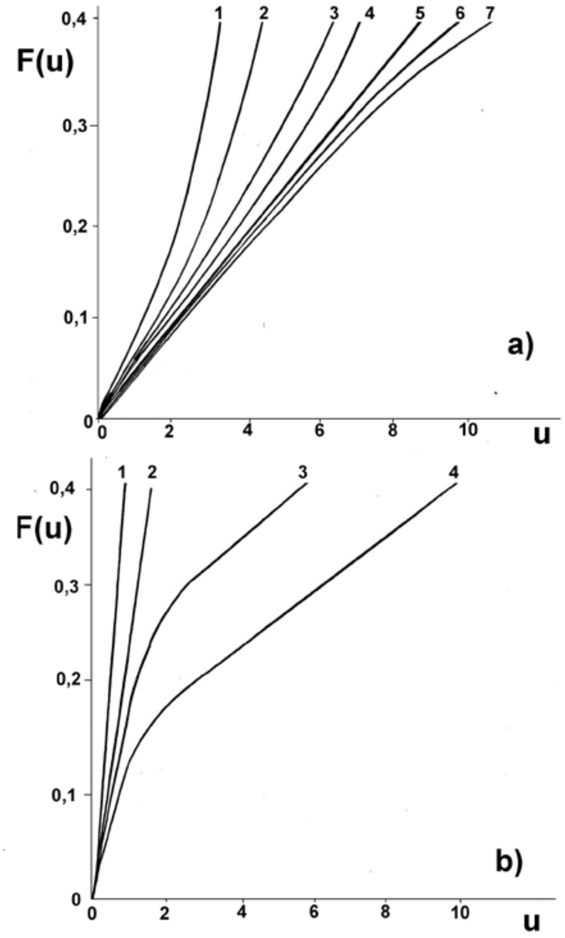

Fig. 1 The effect of surface impurities content (i.e. the parameter value) upon the shape of kinetic curves of hydrogen permeation through metals. $Jt/J\infty$ are plotted in the functional scale F(u), where $u = Dt/L^2$.

a) Bi parameter = $k_{eff}L^2/D=5$

| No | α |
|---|---|
| 1 | -10 |
| 2 | -5 |
| 3 | -1 |
| 4 | -0.5 |
| 5 | 0 – undisturbed diffusion |
| 6 | 0,2 |
| 7 | 0,5 |

b) Bi parameter = $k_{eff}L^2/D=1$

| No | α |
|---|---|
| 1 | -0,5 |
| 2 | 0 – undisturbed diffusion |
| 3 | 0,2 |
| 4 | 0,5 |

If the chemical reaction (with hydrogen involved) occurs on the membrane entrance side (at the exit 3ide, the boundary conditions are of the first kind), and the reaction is evaluated according to the amount of hydrogen flow at the membrane exit, then the reaction kinetics distortion due to slow hydrogen diffusion over the bulk of the metal is described by the following expression (a convolution type equation):

$$J(t)=C_{S,\infty}Q(t)+\int_0^t\left(C_{S,0}-C_{S,\infty}\right)\frac{\partial F}{\partial t}Q(t-\tau) \qquad (9)$$

or in the normalised form:

$$J(t) = Q(t) - \alpha \int_0^t \frac{dF}{dt} Q(t-\tau) d\tau \qquad (9a)$$

where J(t) is the amount of molecular hydrogen flow at the membrane exit changing with the time (the kinetic curve of hydrogen permeation through a metal membrane when the chemical reaction with hydrogen involved takes place at the entrance side of the membrane). Q(t) is the kinetic curve of hydrogen permeation under boundary conditions of the first kind at the membrane entrance. This function is defined by the hydrogen diffusion mechhism over the bulk of the metal, and the real structure of the membrane material must be taken into consideration. Therefore, one need to solve the initial differential equations describing the diffusion in: a) homogeneous media, b) defective media, c) stratified media and etc. In the process of mathematical simulation we assume that Q(t) is defined by the solution of the equation (3). $\frac{dF}{dt}$ is the velocity of surface process at the membrane entrance which results in the hydrogen concentration change in the near-surface layers of a metal (e.g. when hydrogen reacts with carbon).

It should be stressed that if the hydrogen bulk diffusion mechanism is known, then with the Predholm equation ofthe first kind (9) is solved relatively $\frac{\partial F}{\partial t}$, it is possible to define the surface reactionskinetics taking into account the kinetic curve shapes which describe the hydrogen permeation process.

We used marthematical simulation to analyse the results of the model suggested. For calculations it was assumed that at the entrance side of the sample the process which Is formally described by the first order chemical reactions is taking place. In the normalised form:

$$F(t) = \exp(-K_{eff}t) \qquad (10)$$

where $K_{eff}$ is the efficient velocity constant of the surface process. At the membrane exit there's boundary condition of the first kind: C(L,t)=0, where L is the membrane thickness. Moreover, we suppose that hydrogen diffusion occurs in a homogeneous medium, i.e. the hydrogen permeation kinetics is described by the homogeneous medium permeation equation under the boundary conditions of the first kind. Then,

$$Q(t) = Q_\infty \left[ 1 + 2\sum_{i=1}^{\infty} (-1)^n \exp\left( -\frac{n^2\pi^2 Dt}{L^2} \right) \right] \qquad (11)$$

It must be stressed that in this case we assume that the hydrogen concentration on the contaminated entrance membrane side changing with the time is described by the equation:

$$\frac{\partial C_S}{\partial t} = -k_{eff} \left( C - C_\infty \right)\Big|_{x=0} \qquad (12)$$

It is clearly seen that this expression coinsides with the linear boundary conditions of the third kind [2]. Actually, in the dimensionless form:

$$\frac{du}{dt} = Bi(1-u) \qquad (13)$$

where $Bi = \frac{k_S L}{D}$ is the Bio’s criterion, and u=C/$C_0$.

The solution of this equation is

$$1 - \frac{C(t)}{C_\infty} = \left( 1 - \frac{C_0}{C_\infty} \right) \exp(-k_S t) \qquad (14)$$

Nevertheless, in contrast to the ordinary form of linear stationary boundary conditions of the third kind the C(t) is normalised in relation to the initial hydrogen concentration, $C_{S,0}$. The normalization in this very case is performed relatively the stationary value of hydrogen concentration, $C_{S,\infty}$, at the membrane entrance. Therefore, the equation (9), (11) and (12) taken into consideration, describes the hydrogen permeation kinetics for both cases of purification and contamination of the entrance membrane surface. For example, if the membrane surface is coated by one layer of a chemically active impurity, then hydrogen concentration on the membrane surface increases with the time:

$$C_S=C_{S,0}[1-\exp(-K_S t) \qquad (15)$$

On the contrary, if the surface is initially absolutely pure and then It is contaminated, it results in

$$C_\infty= C_{s0} \exp (-K_S\, t) \qquad (16)$$

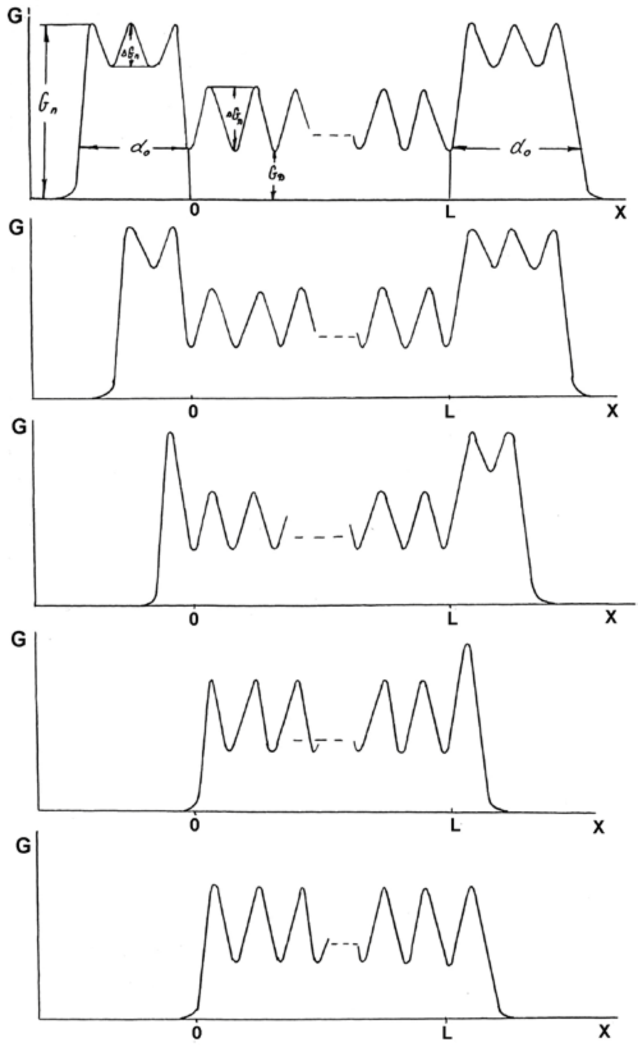

Fig. 2 The power diagram of the membrane cross-section the surface of which is covered -with homogeneous polymolecular layers (G is Gibbs free energy, x - coordinate, $\Delta G_n$ and $\Delta G_D$ are the potential barrier values for hydrogen diffusion over the surface impurities and the bulk od the metal, correspongingly, $G_n$ and $G_D$ are free energies of hydrogen solution in the surface layer of impurities and in the metal), t are different times of diffusion ($0 \leq t \leq \infty$).

During the mathematical modelling we studied the effect of the absolute value of α parameter, its sign and the velocity constant value of a chemical reaction of the first order at the memberane entrance upon the kinetic curve shapes of hydrogen permeation. The analysis of the kinetic curves was performed with the help of functional scales method [4]. For this reason within the frame of homogeneous diffusion under ordinary boundary conditions of the permaetion method (conditions of the first kind) the diagrams were calculated. The scale on the ordinate axis is chosen in such a way that for a classical diffusion mechanism the experimental curve of hydrogen permeation presents itself a straight line coming out of the coordinates origin, the slope angle tangent of which is exclusively defined by the $D/L^2$ parameter value. If the presence of a chemical reaction distorts the kinetic curve, then its plotting will real a deviation from the linear dependence; the character and the value of this deviation allow to make certain criteria of a chemical process occurence.

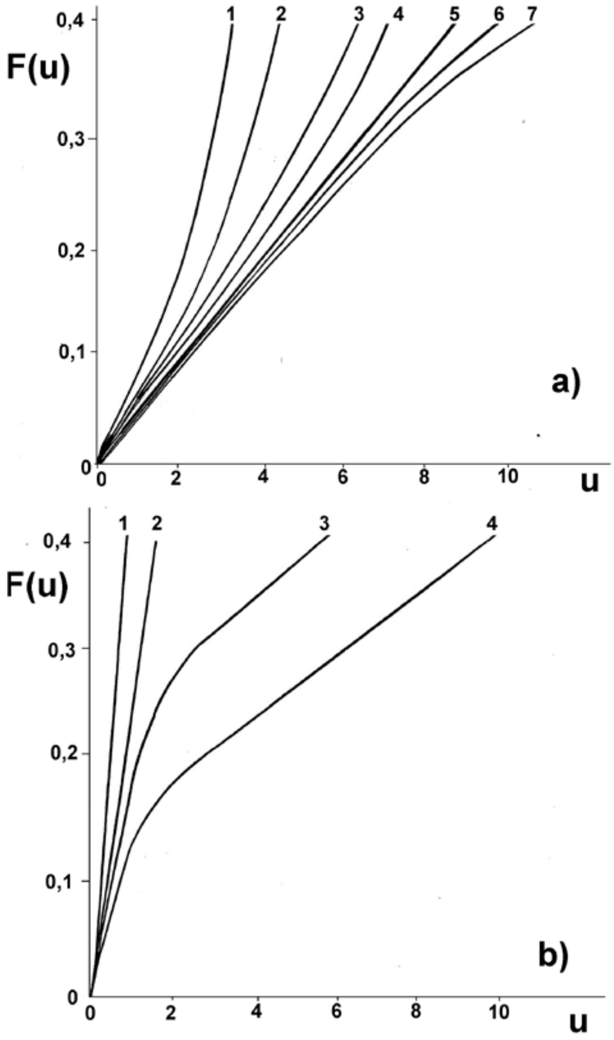

Fig. 3 - The effect of the membrane surface homogeneous poly layer impurities thickness, m, upon the kinetic curves of hydrogen permeation through the membrane, the curves are plotted in the functional scale $\left(\frac{K_{eff}L^2}{D}=1\right)$ where $K_{eff}$ is the effective velocity constant of the last impurity layer distruetion, m is the number of monolayers).

| No | m |
|---|---|
| 1 | 0 |
| 2 | 1 |
| 3 | 2 |
| 4 | 3 |
| 5 | 4 |

To illustrate this Fig.1 shows the influence of α parameter upon the kinetic curve shapes plotted in the functional scale. As seen from the figure, for short periods of diffusion the chemical reaction doesn't practically affect the curve shape, and consequently the bulk diffusion coefficient ($D=L^2 tg\varphi$) can be defined on the initial part of the curve. When $\alpha>0$ the surface is contaminated, and the flow decreases for longer time periods, while for $\alpha<0$ the surface is purified, and the flow acquires the stationary value faster than it in the classical diffusion when the time periods are prolonged. When the surface is purified the effective diffusion coefficient calcaulated by means of the linear variant of the least squares method on the basis of the data available or defined by the time delay is lower than the true coef-fient of hydrogen diffusion over the bulk of the material. On the contrary, if the surface is contaminated, then the linear variant of the least squares method gives the higher value of the effective diffusion coefficient.

The comparison of Fig. 1a and Pig.1b shows that the lower surface reaction velocities (lower $K_{eff}$) the more is the affect upon the kinetic curves by the surface reactions. For one and the same absolute α value, the purification process has stronger influence upon the kinetic curves than contamination.

The comparison between the criteria of the model given and the criteria of other models reveals that for $\alpha<0$ the present model is referred to the class of diffusion models: with an irreversible chemical reaction of the first order (diffusion perculiar to the radioactive decay of a dif-fusate). When $\alpha>0$ the present model is referred to the class of parallel or dissociative diffusion models. Actually, it is impossible to divide the models within one class according to the kinetic curve shape, and to have perfect understanding of the process mechanism one should take into account the data of other physico-chemical analytical methods.

Now, let us consider the case when a chemical reaction of the first oeder between hydrogen and an impurity occurs both at the entrance and the exit of the membrane, reaction velocity constants are different at the entrance ($K_1$) and at the exit ($K_2$). We assume that at the entrance the reaction velocity $f=\frac{dF_1}{dt}$ and the hydrogen concentration change $f_1=\frac{1}{k_1}\exp(-k_1t)$; at the membrane exit we have $f_2=\frac{dF_2}{dt}$ and $f_2=\frac{1}{k_2}\exp(-k_2t)$, correspongingly. Then, to describe the normalised flow at the membrane the convolution equation should be applied twice: at first, the reaction kinetics distortion due to the diffusion delay is to be determined:

$$\tilde{J}_t^* = \int_0^t f_1(\tau)K_1(t-\tau)d\tau \qquad (17),$$

where $K_1$ the equation nucleus is based upon the solution of the problem for the case of diffusion in a homogeneous medium under ordinary boundary conditions of permeation method. Here, the equation is similar to the equation (9). Secondly, we must take into account the distortion of the diffusion and the reaction at the entrance due to the chemical reaction occuring at the membrane exit

$$\tilde{J}_t = \int_0^t f_2(\tau)K_2(t-\tau)d\tau \qquad (18)$$

where the equation nucleus $K_2$ based on the $\tilde{J}_t^*$ function.

In general, the solution of the problem of hydrogen permeation with a chemical reaction of the first order occuring at the entrance and exit sides can be reduced to the diffusion problem of a permeation through a flat membrane with in-homogeneous boundary conditions of the third kind. Then, $Bi_1=\frac{k_1L}{D}$ and $Bi_2=\frac{k_2L}{D}$ should be chosen as Bio's criteria.

It has been already mentioned above that the difference between the traditional approach and the one suggested in the present paper is in choice of hydrogen concentration on the membrane surface in stationary state as the normalising factor. As a result, the solution will describe the hydrogen permeation for the cases of contamination and purification of the entrance or/and exit surfaces.

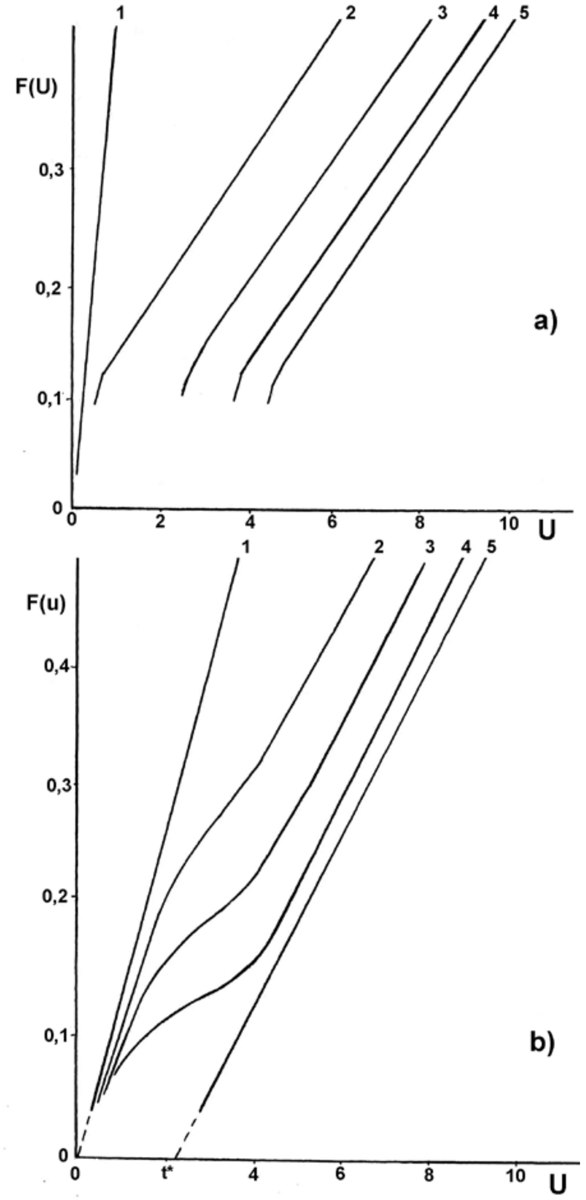

Fig. 4 The effect of the membrane surface segment polylayer impurities upon the kinetic curves of hydrogen permeation through a membrane, the curves are plotted in the functional scale (instant etching of the last layer).

| No | m | $S_i/S$ |
|---|---|---|
| 1 | 0 | 1 - pure entrance surface |
| 2 | 1 | 0,5 |
| 3 | 2 | 0,5 |
| 4 | 3 | 0,5 |
| 5 | 4 | 1 - homogeneous polylayer coverage of the surface |

## 5. Hydrogen involved into popochemical occurring on the membrane surface

We have already studied the case when the impurity is distributed over the membrane surface like a monolayer or it covers onle a part of the surface. In natural conditions, polylayer coverages may exist. The reaction of hydrogen with a coverage (e.g. with carbon) result in a gaseous reaction -product formation and etching the layer which gradually becomes thinner (i.e. hydrogen stimulates a surface topochemical reaction which is called "reaction of a contracting plateLet us assume that a metal surface is covered by a polylayer carbon with the thickness $d=m\Delta$, where m is the number of monolayers, and $\Delta$ - one monolayer thickness. Fig.2 presents the power diagram of hydrogen solution and diffusion in such a membrane. We believe that hydrogen is practicall insoluble in the impurity layer, i.e.

hydrogen can't permeat through a membrane up till the surface is purified. Futher, hydrogen Is supposed to react with carbon with a constant velocity and, consequently, the layer thickness diminishes with a constant rate, $\upsilon$. Then, the time required for the polylayer ooverage disappearance is $t=m\Delta/\upsilon$. If the last monolayer is etched "instantly", then we have the following boundary conditions:

$F=0$ for $t<t^*$

$F=C_0$ for $t>t^*$

If the last monolayer etching develops with the time according to the mechanism mentioned in section 4 of the present paper, then we have the following boundary conditions: $F=0$ for $t<t^*$, or $F\sim C_0^*$, where $C_0^*$ drfined by the hydrogen solubility in carbon $F=[(C_\infty-C_0)/C_\infty]\exp(-K_{ef}t)$ for $t > t^*$, where t is the time of diffusion experiment.

In the first case, the J(t) curves plotted in the functional scale present themselves straight lines with the slope angle tangent. The lines are defined by the value of the bulk diffusion coefficient. But these lines are displaced towards longer periods for one time section t* (the thicker the coverage the greater displacement is), see fig.3. In the second case, the plots have curves which are also displaced by t* towards longer periods of time.

Now let us consider hydrogen permeation through a membrane the separate segments of which are covered with polylayers of a chemically active impurity with the rest part of the surface being absolutely pure. This mechanism can be formalised within the frame of the transmembrane transfer models which use two independent channels. The diffusion coefficients in each channel are equal, but while one channel (its contribution is defined by the segment of pure surface $S_1/S$) is characterised by the non-disturbed diffusion with the boundary conditions of the first kind, the second channel (its contribution is $S_2/S$; $S_1+S_2=S$, S is the membrane surface area) has the polylayer coverage at the entrance which reacts with hydrogen forming a volatile product. On the whole, exit surface of the membrane there are boundary conditions of the first kind.

To illustrate this Fig.4 presents the kinetic curves of hydrogen permeation process which are plotted in the functional scale. They are calculated within the frame of the transmembrane transfer two-channel model (the contribution of each channel to the total flow is 50 per cent), undisturbed diffusion mechanism takes place in the first channel, while "thick" impurity layers etching followed by the surface purification occurs in the second one. It is clearly seen that the thicker the coverage of the contaminated segments the stronger is the distortion of the kinetic curves while the J(t) graphs ploted in the functional scale acquire S-form. For short periods of time the staight segment is preserved. Using the slope angle tangent of this straight segment it is possible to define the undisturbed diffusion coefficient. Besides, this segment describes the hydrogen diffusion kinetics through the pure channel. The diffusion process in this channel reaches the stationary state rather quickly. Further increase of the flow becomes possible only after the contaminated segment has been purified. The flow increase is described by D again as for the classical mechanism. The straight segment extrapolation against the time axis gives the time value for the end of the etching.

Similar shapes of the kinetic curves were observed during the study of hydrogen permeation through nickel at high temperatures.

## 6. Summary and conclusions

Some mathematical models included into the automatical processing system DIGS [5] applied for the results of the diffusion experiments were studied. This system is a part of the scientific work which is carried put with the help of the experimental complex "DOM-1". The main attention is given to that class of the models which take into account the near-surface impurity effects upon the kinetics of hydrogen permeation through metals. Such real physical situations as inhmo-geneous element composition of the surfaceremaining constant during the diffusion process, or changing due to impurities diffusion, phase transitions in the bulk of the metal, or due to chemical reactions between hydrogen with surface impurities have been analysed. The impurities on different membrane sides may have either homogeneous or inhomogeneous chemical composition. They can be either chemically active or passive in relation to hydrogen. Besides, the impurities may cover the whole area of the surface or only a certain part of it having the form of a monolayers or polylayers.

Different physical situations result in various mathematical diffusion models which however can be united within the frame of one methodological approach. With the help of mathematical modelling method it is shown that the surface inhimoge-neity, the presence of active or passive impurities result in the distortion of the kinetic curves of hydrogen permeation. The distortion is especially vivd when the kinetic curves are plotted in the functional scale. It is illustrated that in number of cases, the permeation method can be used to calculate the compound surface reactions and their parameters, and to determine their type as well. The curve shapes are determined by extreme situations: parallel diffusion or that one occuring at the presence of the irreversible chemical reaction between hygrogen and metal; Here, much depends upon the reaction tendency, i.e. whether it is directed either towards purification or contamination. In some cases, it is impossible to differentiate the models according to the shape of the kinetic curves, and to find out the true transport mechanism one should study the dependence of the diffusion parameters upon the temperature, hydrogen partial pressure, membrane thickness, and use different methods to control the surface element composition, e.g. Auger-electron spectroscopy [6]. The modelling results give the evidence that in contrast to the hydrogen atomisation - association reaction limiting the hydrogen permeation process at low temperatures, chemical reactions between hydrogen and such impurities as carbon, oxygen, sulphur become dominant only at high temperatures. For some conditions the process of chemical conversion may become so intensive that hydrogen permeation through a membrane into a reciever may completely stop.

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