

A FULL SCALE STUDY OF GAS DIFFUSION IN VACUUM EQUIPMENT MATERIALS. 4. HYDROGEN PERMEATION THROUGH NICKEL MEMBRANES HAVING DIFFERENT ELEMENT COMPOSITION AT THE EXIT SURFACES

1. Introduction

In the previous works of the scientific programme it has been experimentally [1] and theoretically [2,3] proved that mass-spectrographic methods defining gas flows and methods controlling the composition of surface elements should be used together to provide efficient investigation of gas diffusion in solids. The main reason which stimulated the transport processes studying is that surface impurities or impurities in the near-surface layer of a metal may considerably change the hydrogen permeation kinetics.

The present paper is devoted to the studying the kinetics of hydrogen permeation through nickel membranes having different surface element composition. The main attention is paid to displaying the characteristics of the "DOM-1" complex from the point of view of Auger-electron spectrograph method application to control the element composition of the membrane exit surface during the diffusion experiments.

The authors pursued the following aims:

- a) elaboration of nickel membrane surface purification methods and preparation of such membranes that would contain predetermined surface element composition;
- b) qualitative and quantitative evaluation of nickel surface composition and studying its changes caused by hydrogen permeation;
- c) to define the ways how certain kinds of impurities affect the hydrogen-nickel interaction parameters, the kinetic curves of hydrogen permeation, types of the temperatures dependence of hydrogen diffusion parameters.

The experiments on hydrogen permeation were carried out at 473 - 993K, hydrogen partial pressure was 1000 - 10 Pa thickness of membranes was 2,0 mm and 0.8 mm, the initial element composition of the exit surface included Ni, S, C; Ni, S; Ni. Bank models from the DIGS system [3, 4] were used for the data processing. It is found that hydrogen permeation through a nickel membrane may result in either purification or contamination of membrane surfaces, depending upon the experimental conditions. The results obtained with the help of both Auger-analysis and the diffusion experiments showed the similarity of changes of surface element composition.

2. The methods and equipment

Fig.1 presents the schematics of "DOM-1" complex used in the experiments on hydrogen permeation through nickel with simultaneous control of the membrane exit surface. The installation consists of the exit and inlet chambers which are divided by the membrane studied. The membrane is fixed by means of welding in argon atmosphere. The diffusion cell heater ensures the temperature range from 300 K to 1270 K. The temperature was measured by the Pt-Pt-Rh thermocouple. The temperature gradient over the membrane diameter measured by five thermocouples 0.5 K/mm. The experimental temperature range was controlled automatically with deviation ± 0.5 K.

The vacuum system of three-stage oil excluding evacuation includes zeolite magnetic discharge pumps. One of these pumps was used for regeneration of primary high-vacuum pumps and for preliminary pumping down the whole system. As a result, the background hydrogen pressure was 1×10^{-3} Pa both in the inlet and exit chambers of the diffusion cell.

The purifying and gas inlet system includes a hydrogen leak (palladium-silver-filter), an oxygen leak (silver filter) and a piezoelectric ceramic leak. The hydrogen and oxygen leaks are used to inlet the spectrochemically pure gases within the pressure range from 10^{-2} to 10^{-7} Pa. The mass-spectrographic detecting system based on omegatron detectors provides the possibility to

define the gas flow value after the corresponding calibration, to measure the residual pressure both in inlet and exit chambers, and determine the kinetic curve shape. The partial pressure of residual gases was measured with the accuracy of $\pm 10\%$.

The diffusion cell is at the device which allows to place the membrane in the focal plane of the power analyzer. The equipment includes the automatised Auger-spectrometer which is based on the power analyser of the cylinder mirror type. Its power resolution is 0.2%, the relative aperture is 2% from 4π , the synchronous detector sensitivity is $10^{-3} - 100$ mV [5]. Polycrystal samples of super pure nickel made by vacuum melting were used for the investigations. The thickness of samples is 2 mm and 0.8 mm, the diameter is 26 mm. The content of basic impurities (at%): Co - 0.130, C - 0.07, S - 0.04. During the experiment the focus of the Auger-spectrometer was adjusted by means of the inlet displacement device. The Auger analysis was performed for exit surface of the membrane placed in the analyser focal plane.

While calculating the surface area covered by impurities it was assumed that the object of investigation presents itself a thin film which covers a massive substrate. The film contains both an impurity element atoms and atom mixture of the impurity element and the substrate as well. The, the area of nickel surface covered by an impurity element A and the coverage thickness d, can be calculated according to the formulae (1 - 3) [6]:

$$\frac{\varphi_a \left\{ 1 - \exp \left[-1,35 \frac{a_A}{\lambda_A(E_0)} \right] \right\}}{1 - \varphi_A \left\{ 1 - \exp \left[-1,35 \frac{a_A}{\lambda_A(E_1)} \right] \right\}} = \frac{1 + r_A(E_A) \frac{I_{AA}}{I_1}}{1 + r_1(E_A) \frac{I_1}{I_{11}}} \quad (1)$$

where $\lambda(E)$ is the length of the free path of Auger-electrons with E_{eV} energy; E_0 and E_1 are Auger electron energies obtained due to the surface (S) and substrate (Ni) contamination, correspondingly; I_A and I_1 are line intensities of the Auger spectrum obtained due to the impurity element and the substrate which is not fully covered by the monolayer of A element; I_{AA} and I_{11} are the line intensities produced by pure standards; r is the backscattering coefficient taking into account the electron backscattering contribution into the Auger flow formation.

Nickel surface area covered by sulphur is calculated according to the formula (1):

$$\varphi_{SNi} = 0,45$$

The degree of nickel surface filling by sulphur and sulphur film thickness are calculated according to the following formulae:

$$\frac{I_S}{I_{N2}} = \frac{2,44 [1 - \exp(1 - 1,616d_s)]}{\exp(-0,689d_s)} \quad (2)$$

$$\frac{I_S}{I_{Ni}} = \frac{0,93\varphi_{SNi}}{1 - 0,19\varphi_{SNi}}$$

where I_S is the peak-to-peak Auger-signal intensity of sulphur; I_{Ni} - Auger-signal intensity of nickel; φ_{SNi} - the degree of filling of nickel surface by sulphur.

The experiments on hydrogen permeation through nickel membranes were carried out under continuous pumping down the exit chamber. Before the experiment, the membrane was degassed by means of heating in super-high vacuum at the temperature 50° more than the diffusion experimental temperatures. The sample was cooled down to the working temperature and the partial content of residual gases was defined both in the inlet and exit chambers. The element composition of the membrane exit surface was also analyzed. At the starting moment the inlet chamber was filled with oxygen (pressure range is 16 - 900 Pa) up to the predetermined value of partial pressure (the filling time is less than 1 sec). During the experiment the mass-spectrometer in the inlet chamber registered the hydrogen partial pressure changes with the time. After diffusion reaches the stationary state the membrane exit surface was analyzed by the Auger-method.

For each temperature the stationary state curves and the ones describing hydrogen flow lowering down after hydrogen evacuation from the inlet chamber were plotted.

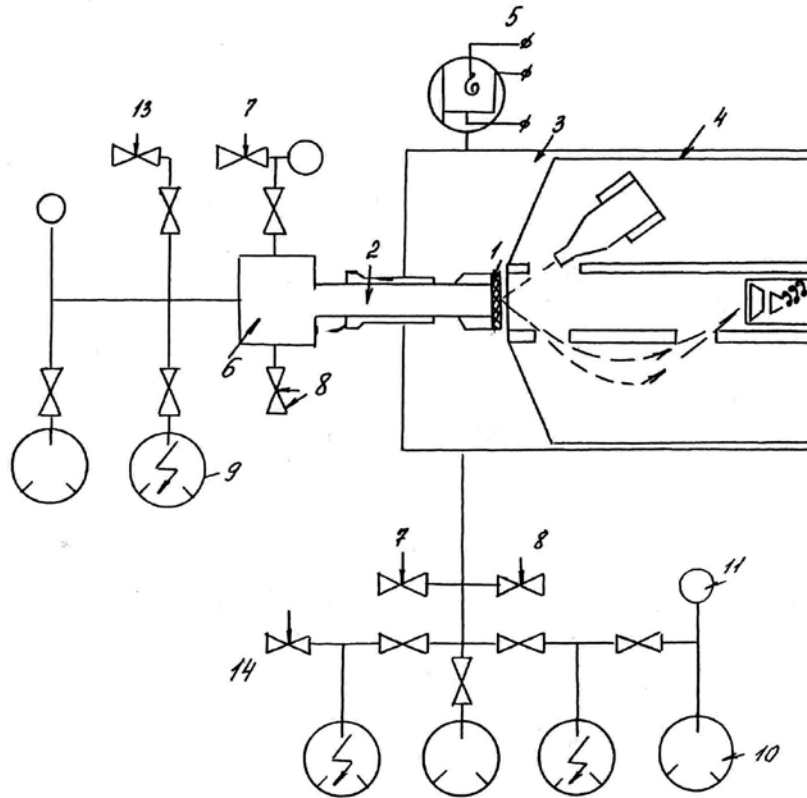


Fig.1 The experimental installation schematics: 1-sample, 2 - inlet chamber, 3 - exit chamber, 4 - power analyzer, 5 - mass-spectrometer, 6 - sample displacement device, 7 - hydrogen leak, 8 - oxygen leak, 9 - "HORD-250" pump, 10 - zeolite pump, 11 - manometer, 12 - vacuum valve, 13 - helium leak, 14 - piesoceramic (or needle) leak.

The diffusion experiments start from $T_{\max}=993\text{ K}$ and then the temperature is lowered (at each step by 50°) down to $T_{\min}=473\text{ K}$.

Primarily, the diffusion coefficient was estimated according to the following formula:

$$D = \frac{L^2}{7,19\tau_{1/2}} \quad (4)$$

where $\tau_{1/2}$ is the time when the flow reaches the value $J_t=0.5J_\infty$, where J_∞ is hydrogen stationary flow through membrane, L is the membrane thickness.

The primary choice of models is carried out with the help of the functional scale [7]. The choice of a model and the final calculation of the parameters and their errors was done by analyzing the kinetic curve shapes of hydrogen permeation with the help of the non-linear variant of the least squares method using the data bank of the DIGS system [4].

The permeation constant for hydrogen flow through nickel is calculated according to the stationary flow value:

$$P_H = \frac{J_\infty L}{S\sqrt{p_{0H_2}}} \quad (5)$$

where S is the membrane surface area, p_{0H_2} is hydrogen partial pressure at the entrance into the membrane.

3. Preparation of nickel membrane having predetermined surface element composition

Sulphur, carbon and oxygen are known to be the main impurities of nickel. Oxygen can be evacuated rather easily by means of a nickel sample heating in vacuum at high temperatures while sulphur and carbon expelling out of nickel surface presents a complicated problem. Moreover, obtaining absolutely pure nickel surface which remains stable during hydrogen

permeation is actually impossible.

To obtain the surfaces with the predetermined element composition such methods as high-temperature vacuum annealing, method of chemical reactions fusing chemically active gases: hydrogen (letting it go over membrane surfaces - annealing in hydrogen (AH) or letting it go to the inlet membrane surface - the hydrogen permeation method (HP)), or oxygen (annealing in oxygen - AO) were used. Besides, some combined purification methods, e.g. consequent membrane processing using HP and AO methods, were of great help.

From the preliminary experiments carried out with the help of Auger-electron spectroscopy and the available data [8] it is known that nickel membrane heating and of course hydrogen permeation result in considerable changes in the surface element composition. For example, when nickel is kept in a high vacuum at the temperature 100° lower than its melting point, the sample surface is completely purified. Nevertheless, when the sample is cooled, the bulk impurities segregate on its surface with following contamination. The similar effects are observed in the experiments on hydrogen permeation when originally pure nickel membrane surface is contaminated during the experiment.

For quantitative description of purification and contamination of the membrane surface let us introduce the notions of the "initial" and "final" surface element composition. The first one (ISEC) denotes the composition expressed by the impurity concentration units in atom per cent defined by the Auger-spectrographic method at the room temperature. The latter one (FSEC) denotes the element composition of the membrane exit side obtained at the stationary conditions of permeation at minimal experimental temperature (473 K). (Auger spectra were registered at the same temperature).

Membranes with the predetermined surface element composition were prepared in the following way: 2 mm thick membrane was fixed in the diffusion cell, then 1×10^{-5} Pa vacuum was created followed by the Auger-analysis of the membrane exit side. The surface Auger-spectrum contains only a carbon line which has been identified as graphite according to its form. The graphite film thickness calculated over the free path length of nickel Auger-electron with the energy of 848 eV turned out to be equal to or over 1.12 nm which is equal at least to five graphite atom layers. After the annealing the inlet and exit chambers and creating the pressure of 1×10^{-8} Pa, the ISEC consists of 19% nickel, 10% sulphur, 71% carbon.

Sample annealing in hydrogen at $T=1075$ K and $P_{H_2} 1 \times 10^{-3}$ Pa didn't cause considerable changes in the surface element composition. The best results were obtained by the hydrogen permeation method; hydrogen flow went through the membrane (the inlet pressure is 4×10^2 Pa, $T=1073$ K, $t=30$ hours). After the three cycles under these conditions carbon was expelled out of the surface - ISEC: 34% nickel, 16% sulphur. Sulphur was expelled by the AO method; the membrane was annealed in oxygen at 10^{-1} Pa pressure, $T=873$ K for 4 hours - ISEC: 100% nickel.

It should be pointed out that all the purification methods aimed at removing impurities out of the surface did not change sulphur and carbon contents in the bulk of the material. It was proved by decreasing thickness of a membrane from 2 mm to 0.8 mm; a new surface had element composition which was identical to the initial one on the membrane surface, $L = 2$ mm, before the chemical treatment,

4. Impurity segregation on nickel surface

Such nickel samples with impurity free surface allowed to study sulphur and carbon segregation during the heat treatment, phase transitions in nickel and hydrogen going through a nickel membrane.

Nickel surface element composition was studied during vacuum annealing and gradual temperature increase from the room value up to 923 K. Each annealing step took 40 min. Auger spectra were measured at the annealing temperature. It is found that sample annealing at temperatures below the Curie point ($T=633$ K) doesn't lead to the surface contamination. In the domain of ferro-paramagnetic phase transition, there was sulphur segregation 93% nickel, 7% sulphur, the degree of nickel surface filling by sulphur is $\varphi_{S_{Ni}} = 0.27$. This segregation is

reversible since the temperature decrease resulted in the disappearance of sulphur peak in Auger spectrum. Carbon segregation in the Curie point domain was not found.

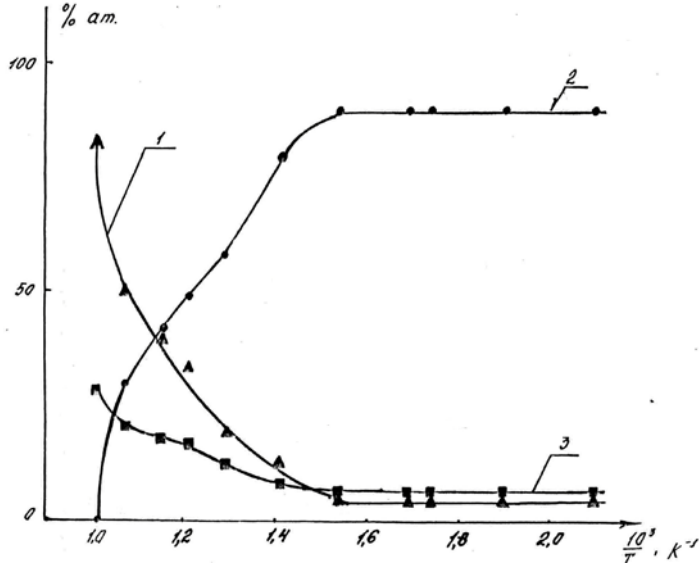


Fig. 2 Change of element composition of nickel sample surface with the temperature.

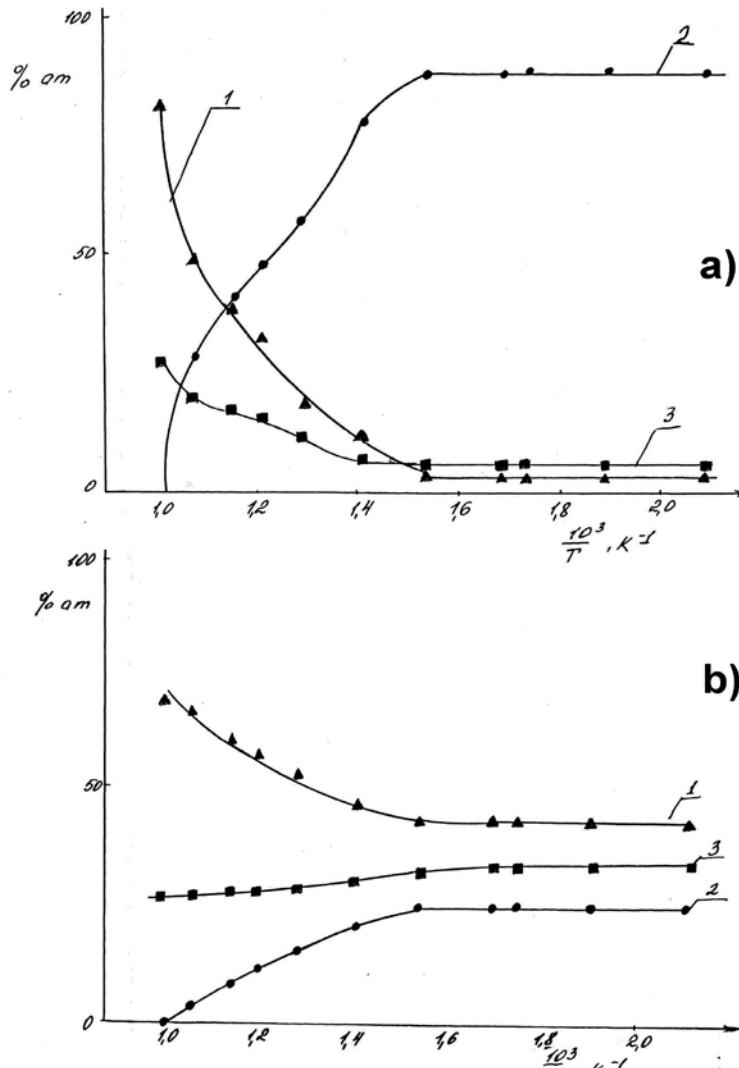


Fig. 3 Change of element composition of nickel sample with the temperature. Surfaces have different ISEC ($L=0,8$ mm, $p_{O_{aH_2}}=10^3$ Pa). ISEC: Ni – 19% at., S – 10% at., C – 71% at; ISEC: Ni – 84% at., S – 16 at.

The experiments aimed at studying hydrogen flow through nickel membrane effect upon sulphur segregation were carried out at 1075 K and 10^3 Pa inlet hydrogen pressure. The Auger analysis of the exit surface after diffusion reached the stationary state showed the following composition: 83% nickel, 17% sulphur. Cooling down to the room temperature caused the change in the element composition: 5% sulphur, 55% nickel, 39% carbon.

In the course of vacuum annealing both element compositions of pure and contaminated surfaces changed. The investigation of membrane surface impurities composition containing nickel, sulphur and carbon (the samples were heated up to 1073 K at each step by 50° , annealing lasted 40 min., 1 hour for each temperature) revealed that at temperature 973 K the membrane surface was carbon free (sulphur expelling is possible at temperatures over 1273 K). It is likely that due to the transformation from the surface into the solid solution the observed effects occur.

Thus, the Auger-spectrographic data show that nickel membrane surface element composition may undergo noticeable changes during vacuum annealing and hydrogen passing through membrane. The impurities containing in the bulk of the material and their segregation tendency caused by hydrogen, prevent obtaining long-standing purity of nickel membrane surface.

5. Nickel surface element composition change during hydrogen permeation constant temperature dependence

Both ISEC and FSEC were measured during the experiments and Auger spectra of the exit membrane surface at each temperature were registered after the kinetic curve had reached the stationary permeation conditions. Figs. 3a and 3b show the surface element composition changes for 0.8 mm thick membrane under different conditions. It is clearly seen that the character of element composition change of the membrane exit surface has strong dependence upon the ISEC. It is revealed in different degrees of contamination within the temperature range of 673 K - 973 K.

The data on hydrogen stationary permeation through nickel membranes show that for 2 mm thick membrane the surface preparation method actually doesn't affect the temperature dependence of the stationary flow and its absolute value. In this case, the flow is proportional to the J_{pH_2} value at pressure over 50 Pa for the whole experimental temperature range. The permeation constant temperature dependence is subjected to the Arrhenius law in the whole temperature range measured.

In the case of 0.8 mm thick membrane both absolute value of J_∞ and its temperature dependence shape depend upon the purity degree of the surface. Figs. 4 and 5 show the temperature dependencies of plotted in the Arrhenius coordinates for the sample having the following ISEC: 84% nickel, 15% sulphur, and 19% nickel, 10% sulphur, 71% carbon, correspondingly. It should be stressed that as a rule, the membrane exit surface final state after the series of the diffusion experiments differs considerably from the initial one (Ref. Figs 3a and 3b). Therefore, the interpretation of the results should include the character of temperature dependencies of carbon and sulphur concentrations on the membrane exit surface (ref. Figs. 3a and 3b).

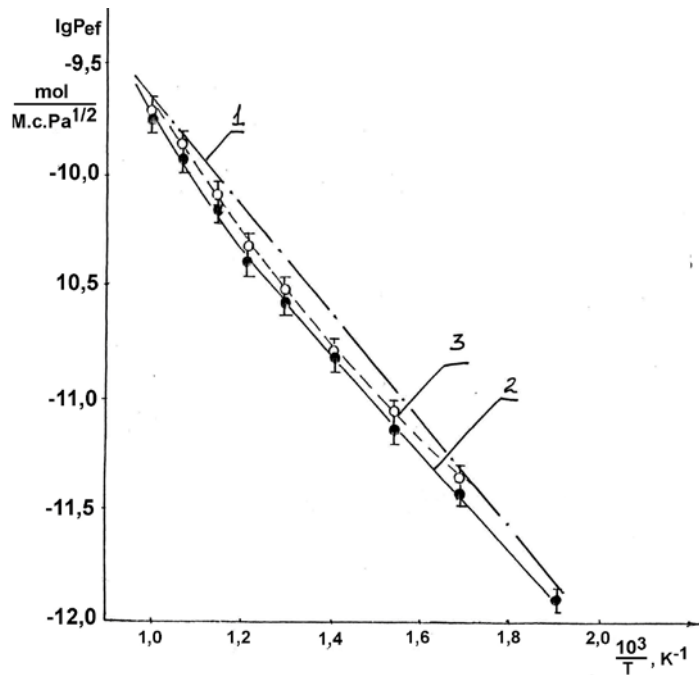


Fig. 4 - The temperature dependence of the effective constant of hydrogen permeation through 0.8 mm thick membrane, ISEC: Ni - 84% at., S - 16% at. 1 - quasibalanced permeation; 2 - experiment; 3 - model.

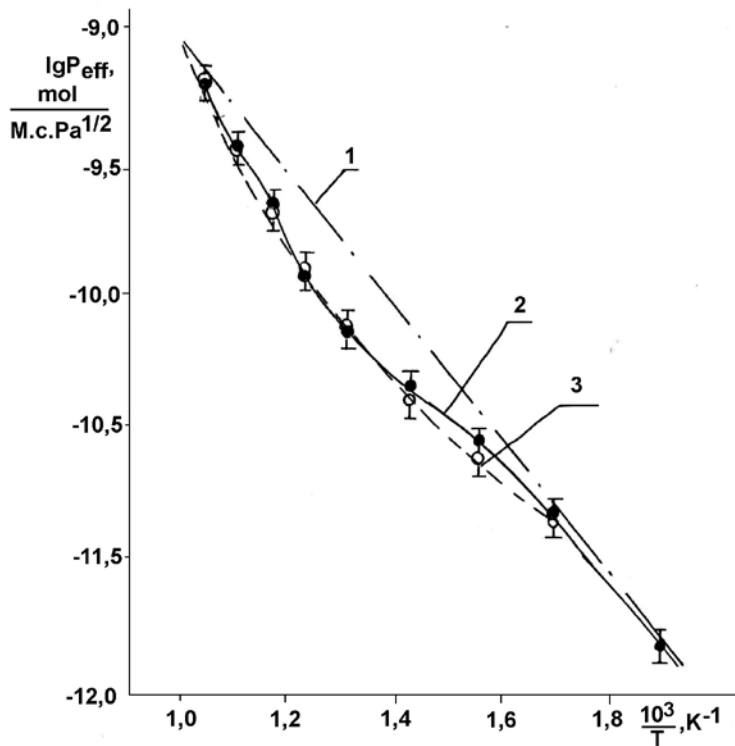


Fig.5 The temperature dependence of the effective constant of hydrogen permeation through 0.8 mm thick membrane, ISEC: Ni - 19% at., S - 10% at., C - 71% at. 1 - quasibalanced permeation; 2 - experiment; 3 - model

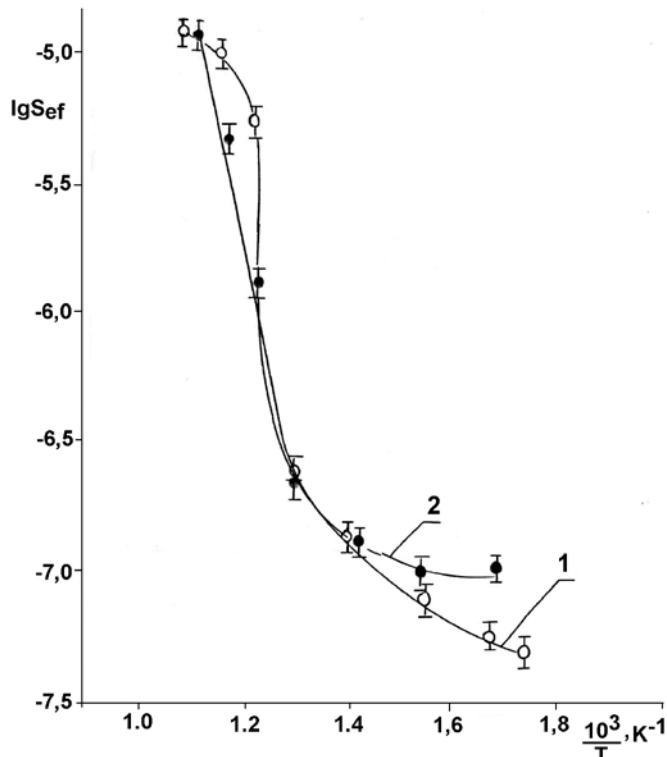


Fig.6 The temperature dependence of the effective coefficient of hydrogen cohesion to nickel. $L=0.8$ mm, $P_{O_{H_2}}=10^3$ Pa. ISEC: Ni - 19% at, S -10% at., C - 71% at.

The temperature dependence of hydrogen flow passing through a membrane having the following ISEC: 19% nickel, 10% sulphur, 71% carbon, has an evident anomaly in the temperature range 643 K - 933 K revealing in the $P_{H(T)}$ graph deflection plotted in the Arrhenius coordinates (Fig.5). The decrease of sulphur and carbon concentrations on the membrane surface leads to the linearity improvement of the plot. First of all, the observed effects should be interpreted qualitatively.

The low-temperature segment of $\log P_{ir} -1/T$ plot has the slope corresponding to the activation energy 47 KJ/mol. This value coincides with the activation energy of the quasi-balanced permeation. The absolute flow values at these temperatures also coincide with the values of flows passing through a "pure" membrane, i.e. they are quasi-balanced. The Auger-analysis demonstrates that at temperatures below 673 K and over 973 K the element composition doesn't change during the diffusion experiment. It should be stressed that under low temperature conditions the dominated impurity is carbon while under high temperature conditions - it is sulphur. Thus, the permeation process is limited by hydrogen diffusion through graphite film under low temperature conditions and it goes through sulphidized nickel under high temperature conditions. Due to the constant surface element composition one may suppose that for this temperature range the number of adsorption centers of molecular and atomic hydrogen and the number of catalytically active centers of hydrogen dissociation-association reaction remain constant during the diffusion experiment, and therefore, the velocity constants of the surface processes do not depend upon the time (but they do depend upon the temperature).

According to the Auger-spectrographic data the surface element composition undergoes essential changes in the temperature range 673 K - 973 K. Therefore, the concentration of catalytic and adsorption active centers depends upon the temperature while the efficient velocity constants of the surface reactions - upon the temperature and time. Since the permeation is limited by a combination of the surface processes, then hydrogen flow through membrane should decrease.

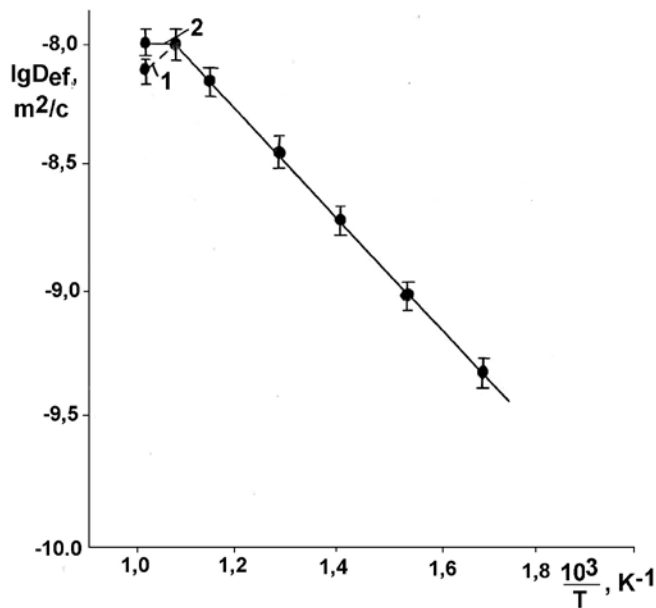


Fig. 7 The temperature dependence of the effective coefficient of hydrogen diffusion in 2 mm thick nickel membrane. ISEC: Ni- 84% at., S-16% at.

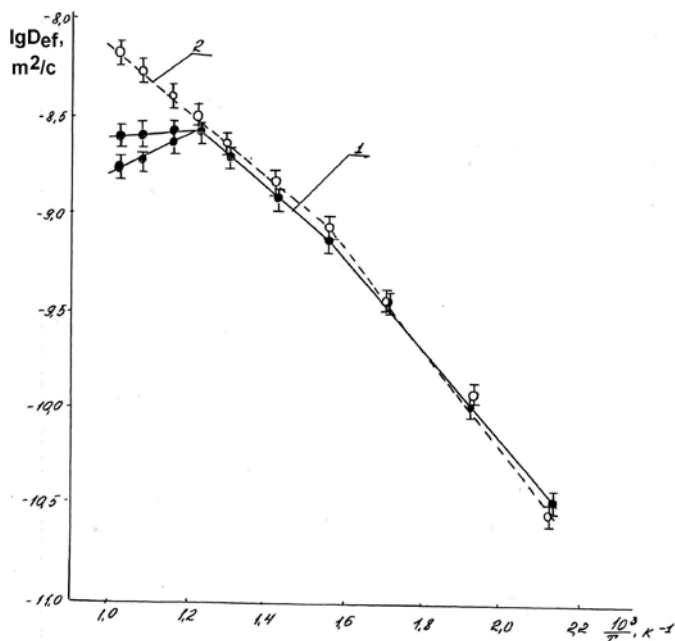


Fig. 8 The temperature dependence of the effective coefficient of hydrogen diffusion in 0.8 mm thick membrane. ISEC: Ni - 19% at%, S - 10% at. C- 71% at. 1 - experiment; 2 - model.

It should be pointed out that similar effects were observed by the authors of [9] when they studied 0.1 mm thick nickel samples but they could not interpret their observations because of the lack of parallel Auger analysis.

Using the data obtained one can estimate the temperature dependence of the effective cohesion coefficient $S_{ef}(T)$ [9], Fig.6.

Now let us interpret the temperature dependence curves of the effective permeation coefficient for the whole temperature range. To perform this, we must assume the following:

1. The membrane surface is inhomogeneous: there are nickel carbon and sulphur segments. The degree of surface filling with i^{th} element is φ_i
2. φ_i changes with the temperature,
3. Inhomogeneous composition of the membrane surface results in several parallel

ways of the transmembrane transport which can be characterised by the values of the local permeation constants F_1 .

Within these assumptions the temperature dependence curves of the effective permeation constants were computed with the help of the non-linear variant of the least squares method according to the formula:

$$P_{ef} = P_{Ni} \varphi_{Ni} + P_{C,S} (1 - \varphi_{Ni}) \quad (6)$$

where $P_{ef}(T)$ is the effective permeation constant defined by the stationary flow value, $p_{C,S}(T)$ - the constant of hydrogen permeation through the segments containing carbon and sulphur, $P_{Ni}(T)$ - the constant of hydrogen permeation through pure nickel segments (P_{Ni} and $P_{C,S}$ are defined from the same parts of the Arrhenius plot which are characterized by $\varphi_i = \text{const}$, according to the Auger analysis data).

It is assumed that permeation constant temperature dependence :

$$P_i = P_{oi} \exp\left(-\frac{E_{Pi}}{RT}\right) \quad (7)$$

where P_{oi} is the first exponential factor associated with the transport paths over the segments contaminated with the i type of impurity, E_{Pi} is the activation energy corresponding to this process. $\varphi(T)$ values are taken from the Auger analysis of the surface under stationary permeation conditions.

The results show that for ISEC: 19% nickel, 10% sulphur, 71 % carbon, $E_{pNi}=52,4$ kJ/mol., $E_{pC,S}=30.6$ kJ/mol, The comparison between the calculated (for these values and taking into account the Auger analysis data) $P_{ef}(T)$ dependencies and those which have been defined experimentally, evidently demonstrates the adequacy of the suggested model (Figs 4 and 5).

Thus, it is found that appearance of the deflections on P_{ef} temperature dependence is associated with the change of the membrane surface element composition with the temperature which in its turn results in a change of permeation local constant spectra.

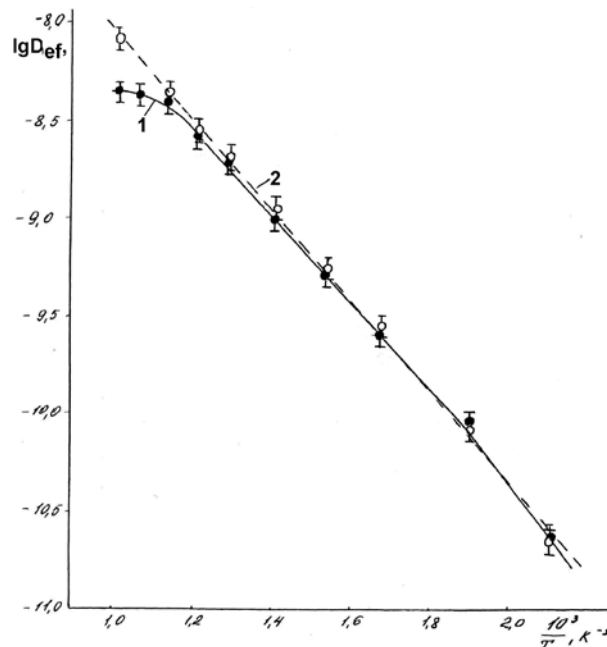


Fig. 9 The temperature dependence of the effective coefficient of hydrogen diffusion in 0.8 mm thick nickel membrane. ISEC: Ni-84% at, 3-16% at.

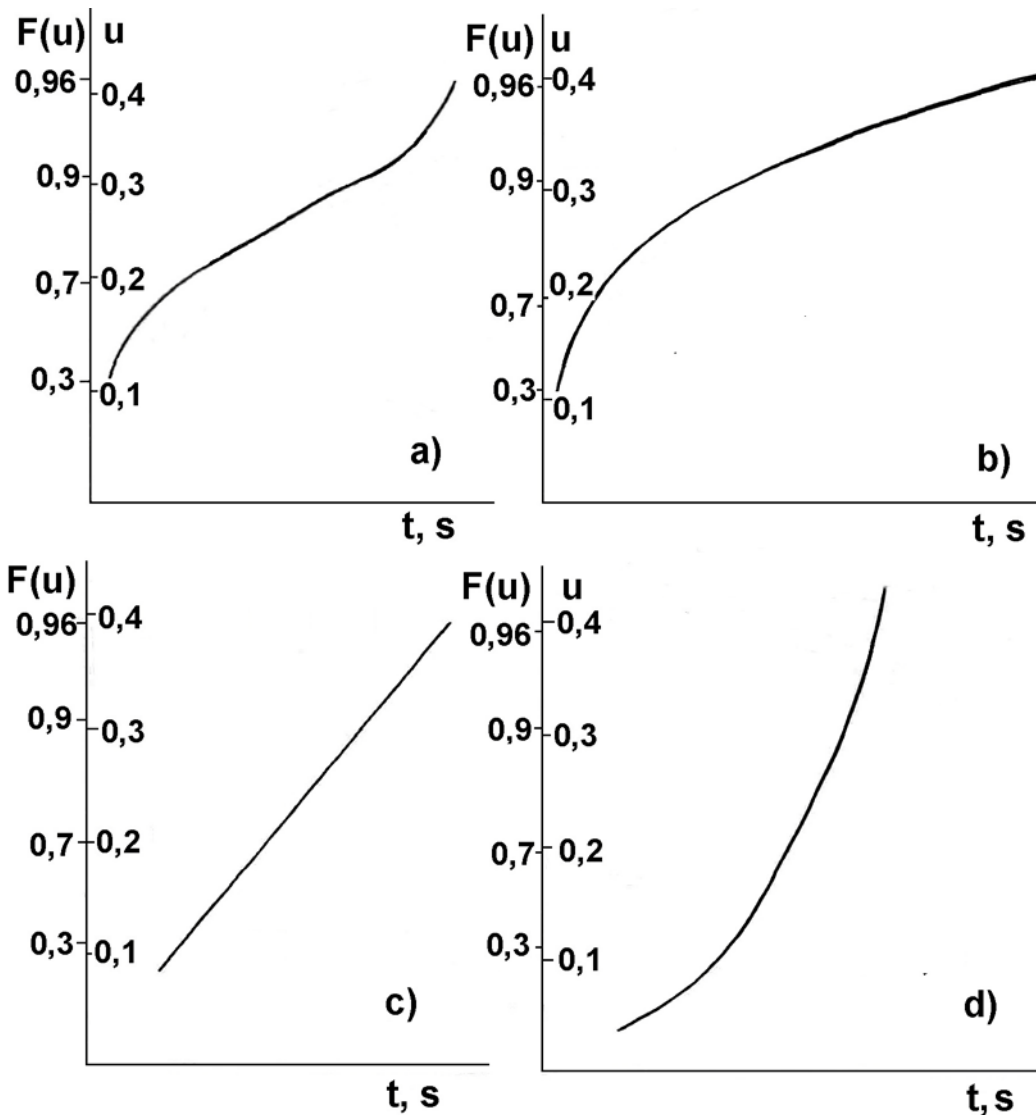


Fig. 10 Typical kinetic curves of hydrogen permeation through nickel. $L=0,8$ mm. The curves are plotted in the functional scale for different temperature interval: a) $T=423 - 623$ K; b) $T= 623 - 823$ K; c) $T=823 - 933$ K; $T=933 - 1023$ K

6. Non-stationary hydrogen permeation through nickel membranes

The effective hydrogen diffusion coefficients in nickel were calculated from the kinetic permeation curves according to the formula (4). D_{ef} temperature dependencies are plotted in Arrhenius coordinates in Figs. 7-9 for different ISEC: nickel-sulphur-carbon and nickel-sulphur. As seen from the figures, there is a linear part for 2 mm thick sample at the temperature below 873 K, The tangent of the slope angle of this linear part was used to calculate the diffusion activation energy. The decrease of hydrogen diffusion coefficient under the temperatures over 900 K is of great importance because maximum at 873 K appears on D_{eff} Arrhenius dependence. As the number of diffusion experiments increases, the more pure the membrane surface is the more the linearity of the plot we observe. For 0,8 mm thick sample, the breakup is observed at the transition from para- into the ferromagnetic nickel phase. Here, the activation energy in low temperature domain is higher than in the high temperature one. The breakup value depends on ISEC: as the carbon quantity decreases on the membrane surface the break up decreases as well.

To find the reasons of D_{ef} decrease under the temperatures over 873 K the kinetic curve shapes were thoroughly analysed. These kinetic curves were measured at different temperatures. The analysis was performed by kinetic curves plotting in the functional scale calculated from the mechanism of undisturbed diffusion over the bulk of the metal under common boundary conditions of the permeation method (the conditions of the first kind). If there's diffusion which

is not disturbed by any surface or bulk processes, then the plot presents itself a straight line coming out of the coordinates origin. If there are chemical reactions with a diffusant taking part, then plots are distorted; these distortions of different curve parts may quantitatively characterise the mechanism of hydrogen permeation.

The experimental curves of non-stationary hydrogen permeation plotted in the functional scale show that though linear dependencies are observed in some cases, the greater part is presented by the distorted plots. The analysis of all the data available allowed to find four main types of the kinetic curve distortions (the graphs are plotted in the functional scale. Fig.10). These anomalies appeared to have close connection with ISEC. For the ISEC: Ni, S (Fig.10a), at the temperature range 423 K - 623 K the $F(u)$ plot presents itself an Increasing function which gives the evidence of the membrane surface purification in the course of hydrogen permeation; at the temperature range 623 K - 823 K there's a linear dependence which allows to describe the process formally by means of the diffusion equation solutions under the boundary conditions of the first kind; at the temperature range 823 K - 933 K the $F(u)$ plot presents itself a decreasing function (surface contamination during the diffusion). For ISEC: Ni, S, C at the temperature range 933 K - 1023 K the $J(t)$ curves plotted in the functional scale have S-form, and it has been already shown in the previous work [3] that it is connected with the transmembrane transport over two parallel channels: over the channel associated with pure surface segments and over the channel associated with "island" segments of the polylayers coverage's (presumably carbon) reacting with hydrogen.

The anomalies described above were registered in both thick ($L=2$ mm) and thin ($L= 0.8$ mm) membranes. In all the cases, the increase of hydrogen inlet pressure results in the decrease or full suppression of kinetic curve anomalies.

Thus, the analysis of permeation curves plotted in the functional scale allows finding the presence of compound chemical reactions on the membrane surface with hydrogen taking part in them. These reactions may either lead to purification or contamination of the surface during the diffusion experiment. However, in contrast to the results of stationary experiments there's no unique correlation between the data of the diffusion analysis under non-stationary conditions. (Here, we mean such analysis which takes into account the processes at the exit, entrance and bulk of the membrane and Auger spectrographic results which provide the information only about the element composition of the exit membrane side).

7. The mechanism of hydrogen permeation through nickel

The present work demonstrates the complicated character of hydrogen permeation through nickel membranes. Here, we should mention the following facts:

- abnormal shape of permeation kinetic curves;
- the maximum appearing at $T=873$ K on the Arrhenius dependence of the effective diffusion coefficient;
- deflections appearing on the Arrhenius dependence of the kinetic curve in the temperature range 623 K - 923 K;
- the breakups on the Arrhenius dependence of the effective diffusion coefficient in the domain of Curie point;
- the dependence of the observed anomalies upon the initial surface element composition, hydrogen partial pressure at the membrane entrance, number of consequent diffusion experiments, etc.

The analysis of the reasons of the observed anomalies was performed by mathematical modeling method using the set of programmers DIGS [4]. Calculations were performed within the model frames: undisturbed diffusion under the boundary conditions of the first kind; the diffusion under linear and non-linear, stationary and non-stationary boundary conditions of the third kind [9]; the diffusion in inhomogeneous media taking into account reversible and irreversible hydrogen capture by the defects [10]; the diffusion under the interaction between the diffusant and the solid matrix or with surface impurities [11]. The comparison between the

experimental data and calculations shows that depending upon the experimental conditions, the following transmembrane transport mechanism fully described in the previous works [2, 3] are possible:

1. The limiting stage is the process of hydrogen passing through the boundary surface phase; the adsorption of hydrogen molecules, hydrogen dissociation-association reaction, atomic hydrogen adsorption, overcoming the near-surface layer with specific diffusion characteristics,
2. The diffusion under the presence of a compound surface element composition which does not change in the course of the diffusion experiment, but with considerable changes of the effective cohesion coefficient.
3. The diffusion followed by the changes of the element composition of both entrance and exit sides of the membrane (contamination and purification are possible).
4. The chemical reactions between hydrogen and "island" poly-layer impurity coverage's decreasing the amount of hydrogen taking part in the transmembrane transport, occur under high temperatures.

Unfortunately, at the present time the solution of the reverse problem - computation of model parameters using the experimental data - is impossible due to the lack of reliable algorithms for diffusion equation solutions under non-stationary non-linear boundary conditions of the 3 kind.

Nevertheless, an attempt was taken up to process the experimental results on non-stationary hydrogen permeation within the frame of a simple approximation: the presence of chemical reactions on the membrane surface. These reactions are of the first order, with hydrogen taking part in them. It may result in either purification or contamination of the surface. It is found out that this simple variant of the model correctly describes the shapes of the most experimental kinetic curves, excluding those having S-form when they are plotted in the functional scale. As a result, such parameters as the contamination degree of the membrane surface in the course of the diffusion experiment, α [3], the effective velocity constant of the surface reaction with hydrogen, k_{ef} , the "true" (bulk) diffusion coefficient, D , have been calculated.

To illustrate this Figs. 8 and 9 present the temperature dependence of D calculated according to the data of non-stationary hydrogen permeation through 0.3 mm thick membrane having different ISEC. As seen in the pictures, the data for D in Arrhenius coordinates in contrast to D_{ef} present themselves straight lines in the whole temperature range studied. The activation energy calculated according to the slope angle tangent of this straight line ($E=35.7 - 0.3$ kJ/mol.) coincided with the activation energy defined with the help of $D_{ef}(T)$ in the low-temperature domain and with the data available [12].

Thus, theoretical concepts on hydrogen diffusion in metals developed in the previous works [2, 3] have been confirmed in the experiments on hydrogen permeation through nickel membranes with different element composition.

8. Summary

The results presented stress the necessity of a serious full-scale study of the diffusion characteristics of vacuum material. Inarticulacy, due to simultaneous application of the hydrogen permeation method and Auger-electron spectroscopy principally new information has been obtained.

The use of Auger spectroscopy allowed preparing nickel membranes with the predetermined surface element composition: H, S, C; H, S; Ni and to study impurity segregation processes which occur under sample heating and chemical reactions. In particular the impurity segregation on the membrane exit side was found during hydrogen permeation through the sample.

A possible explanation of the impurity segregation stimulated by hydrogen could be as follows: it is known [3] that due to the directed movement of charged particles in a substance there appears directed impurity flow, resulting in the material purification. As for the permeation

method, the hydrogen diffusion flow in the bulk of the metal could be the above mentioned flow. The directed flow of charged ions appearing in this case react with such implantation impurities like S and C and stimulates their transport to the membrane exit side. The impurities coming out of the surface produce unbalanced impurity concentrations which could be registered by Auger-electron spectroscopy method.

A problem of great importance is the possibility of compatibility of the diffusion data reflecting the transport characteristics of the near-surface membrane layers and the membrane material used with Auger-analysis data on the membrane exit side. The abovementioned results on hydrogen permeation through nickel show that under stationary permeation conditions (i.e. after the diffusion flow reaches its stationary value and after all the reactions with hydrogen resulting in the change surface element composition, come to an end) these two types of data correspond to each other.

Under non-stationary experimental conditions there's no such data correlation for the two methods of analysis. In some cases, compound chemical reactions occur on the membrane entrance side. These reactions influence the diffusion process but not the Auger spectra of the exit side. Thus, the necessity of further development of the experimental complex "DOM-1" aimed at using physico-chemical and nuclear physical methods of the surface element composition control or composition control of the near-surface layer both at the exit and the entrance sides of the membrane, becomes evident. Nevertheless, even at the present time Auger analysis of the membrane exit surface before and after non-stationary diffusion experiments allows to refer hydrogen permeation process to a concrete physical situation.

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