

# THE NEW APPROACH TO DESCRIPTION OF THE INTERACTION BETWEEN HYDROGEN ATOMS AND DEFECTS OF STRUCTURE IN METALS

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## ABSTRACT

The generalized mathematical model of the hydrogen interaction with metal structure defects has been developed. This model is based on the application of the differential mass transfer equation describing the hydrogen permeation processes in metals. The new boundary condition on input of membrane is introduced. The common equation of the hydrogen current permeation through the steel membrane has been analysed. First it was shown theoretically that maxima on permeation curves were due to the decreasing of dissolved hydrogen concentration in lattice under the influence of hydrogen trapping by metal structural imperfections. By the electrochemical permeation measurements the hydrogen current permeation dependences on time for steel with varying polarization conditions have been studied.

## KEYWORDS

Hydrogen, hydrogen interaction, diffusion, trapping effect, mathematical model, electrochemical permeation method, boundary conditions, defects of structure

## INTRODUCTION

It is well known that diffusible in lattice hydrogen atoms can interact with structural imperfections in crystals (Geld et al., 1979). Such interactions is observed already in pure metals, and especially displays during the adding of inclusions. The presence of hydrogen in defects of metal may be cause a loss of mechanical characteristic of materials. This problem is studied many years, but not all aspects yet remains to be understood (Pressouyre and Bernstein, 1978). McNabb and Foster (1963, 1965) submitted a considerable contribution into the theory of the hydrogen behaviour in metals. They developed a general theory to the describing of the hydrogen diffusion in steel. However, the authors does not take into account the irreversible trapping (MF-model).

They introduced the formal constants of capture and release hydrogen rate and received the differential equation describing the transport and diffusion processes in metals. This equation differs from Fick's second law by the presence of the added item, which takes into account the interaction mechanism. Casky and Pillinger (1975) generalized the MacNabb and Foster's equation for decision the some problems distinguishing by the initial and boundary conditions.

Iino (1982a,b,1985) developed a diffusion model, which is consistent with MF model. The investigations (Iino, 1982a,b) contain the theoretical analysis of reversible and irreversible trapping.

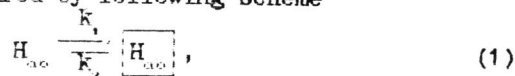
Comparison the experimental data of the hydrogen transport through the metals and results of the mathematical MF-model indicated that the theoretical bifurcation of the kinetic dependence, in spite of numerous measurements, never has not been observed. In practice the permeation curves of hydrogen have a maximum. The time-dependents of the current permeation with various sulfur contents can serve as the typical example (Fig.2 (Iino,1985)). These curves have a obvious maxima. Values the current permeation in maxima and its attained time depends from sulfur concentration. Thus, there is discrepancy between MF-model and real system. Since Iino (1982a,b) in their investigations considered more complicated mechanisms of interaction, he does not obtained the theoretical dependence for current transient with maximum.

For analysis of the hydrogen behaviour in metals Wu (1987) developed a mathematical model differing from MF-theory. Author introduced the new boundary condition on input of membrane. According to this model the trapping is considered only in subsurface layer of metal.

#### MATHEMATICAL MODEL

Below it is represented the results of the analysis of the generalized model of the hydrogen interaction with structural imperfections in metals. It's our point of view this model is free from above mentioned lacks of the Wu's and McNabb-Foster's theories and exact describes the processes taking place in real systems during the hydrogen diffusion through the metals.

Let us consider the influence of trapping behaviour on the hydrogen transport kinetic through the metal membrane. According to the theory of McNabb-Foster (McNabb and Foster,1963, 1965), hydrogen is captured by following scheme



where  $k_1$  and  $k_2$  is the formal rate constants of the capture and release, respectively. This case will be correspond to hydrogen diffusion with traps of one kind or reversible trapping (Iino,1982a,b). In equation (1) the hydrogen captured by

traps is situated in rectangle. By equation (1) the diffusion problem for plane membrane can be written as

$$\partial g / \partial \tau + \partial V / \partial \tau = \partial^2 g / \partial z^2 \quad (2)$$

$$\partial V / \partial \tau = \lambda g - \mu V \quad (3)$$

$$g(z,0) = 0 \quad \tau = 0 \quad 0 \leq z \leq 1 \quad (4)$$

$$g(0,\tau) = 0 \quad \tau \geq 0 \quad z = 0 \quad (5)$$

$$g(1,\tau) = 1 + (\lambda/\mu) \exp[-(\lambda+\mu)\tau] \quad \tau > 0 \quad z = 1 \quad (6)$$

Here  $\lambda = Nk_1L^2/D_H$ ;  $\mu = k_2L^2/D_H$ ;  $g(z,\tau) = c(z,\tau)/c_H^0$ ;  $N$  is the number of traps per unit volume.  $V = N\theta/C_H^0$ , where  $\theta$  is the fraction occupied of  $N$  traps,  $C_H^0$ ,  $D_H$  is the hydrogen concentration and diffusivity in the system, respectively,  $L$  is the thickness of membrane. The non-dimensional parameters  $\lambda$  and  $\mu$  represents the ratio of capture and diffusion constants ( $\lambda$ ) and release and diffusion constants ( $\mu$ ), respectively.

The equation for the current permeation can be written as

$$I(\tau) = (\mu/(\mu+\lambda)) \left\{ 1 + S_{1,2} + (\lambda/\mu) \left[ \exp[-(\lambda+\mu)\tau] + S_{3,4} - S_{5,6} \right] \right\} \quad (7)$$

where

$$S_{1,2} = \sum_{k=1}^{\infty} (-1)^k a_k^{\pm} \exp(-S_k^{\pm} \tau) \quad (8)$$

$$S_{3,4} = \sum_{k=1}^{\infty} (-1)^k \left[ a_k^{\pm} (\lambda+\mu) \right] \exp[-(\lambda+\mu)\tau] / (\lambda+\mu - S_k^{\pm}) \quad (9)$$

$$S_{5,6} = \sum_{k=1}^{\infty} (-1)^k \left( a_k^{\pm} S_k^{\pm} \right) \exp[-S_k^{\pm} \tau] / (\lambda+\mu - S_k^{\pm}) \quad (10)$$

Here

$$a_k^{\pm} = 2\pi^2 k^2 / S_k^{\pm} \left[ 1 + \lambda\mu / (S_k^{\pm} - \mu)^2 \right], \quad (11)$$

and  $S_k^{\pm}$  is the poles of the equation

$$S_k^{\pm} = (1/2) \left[ \lambda + \mu + \pi^2 k^2 \pm \sqrt{(\lambda+\mu+\pi^2 k^2)^2 - 4\lambda\mu\pi^2 k^2} \right] \quad (12)$$

Equation (7) is non-convenient for analysis. That is why the numerical calculations of the kinetic dependences of current permeation versus time with various values of  $\lambda$  and  $\mu$  parameters have been carried out. It is obtained the time-dependents current permeation is distinguished with the changing of  $\mu$  value and have a three typical forms (Fig.1).

For the small values of hydrogen release from traps constant,  $\mu \leq 0,1$  (Fig.1a) the curves of time-dependents current permeation have obvious maxima. With the decreasing of the hydrogen capture rate by traps, i.e.  $\lambda \rightarrow 0$ , maximum is smoothed and in limit the curve  $I(\tau)$  is consistent with classical dependence. The increasing of  $\lambda$  tends to shift the maximum current and its position to short times.

For the large values of  $\mu$  (Fig.1b), when the release rate of the hydrogen atoms from traps is fast, the theoretical time-dependents current permeation have S-form, distinguishing by the steady state current permeation value. In this case the more of value  $\lambda$  the smaller  $I(\tau)$ . Generally, one may judge the current transient dependences versus time qualitatively are coincided with classical case, when the processes of the hydrogen capture and release are absent. These enable to discover the kinetic effects, which is due by the hydrogen interaction with structure imperfections of metals.

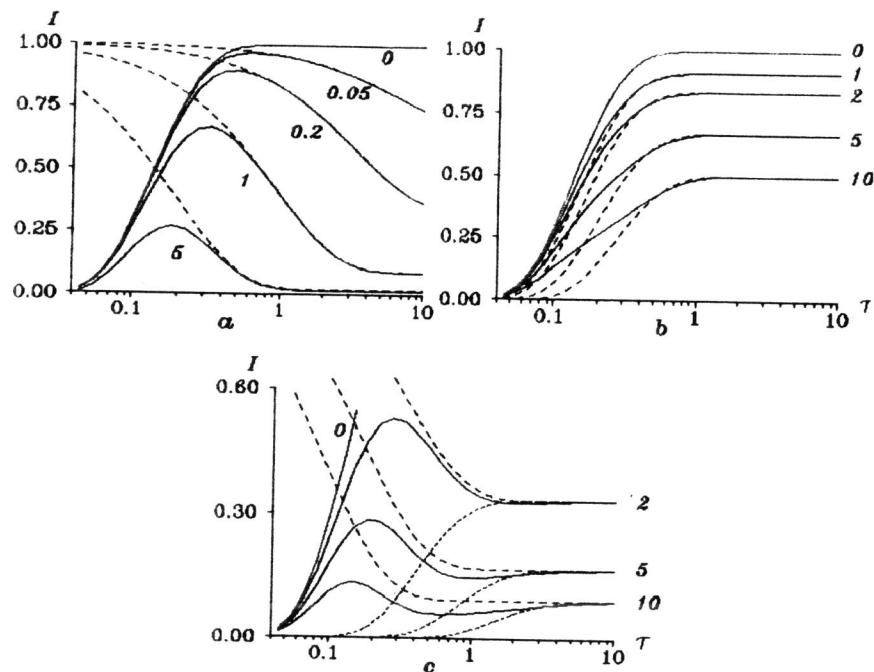


Fig.1. The time-dependents of the current permeation in non-dimensional form. The calculations with Eq.(7) are shown by solid lines; the calculations with approximations (13) and (14) - dashed lines.  $\lambda$  indicated on plots and  $\mu$ : a - 0.1; b - 10; c - 1, respectively.

Finally, the third time-dependents current permeation is observed for average  $\mu$  (Fig.1c). It is shown the curves have a maxima and plateau, moreover the value of plateau is more then the value of current permeation in minimum. The value of the steady state current permeation is increased when  $\lambda$  is increased. The smaller its attained time is the smaller  $\lambda$ . The influence of the hydrogen capture constant by traps  $\lambda$  on the value and time position of the current maximum is analogous to case with the small  $\mu$ .

Thus, the capture and release hydrogen parameters are influenced on the shape of the theoretical current permeation versus time dependences adding to them the extraordinary character (Fig.1). It is shown that the attained time of the current permeation maximum does not depend from  $\mu$  and is defined by  $\lambda$ . With increasing of the hydrogen release rate constant from traps the character of permeation curve is changed on exponential and attained time of steady state is decreased. It should be noted that the theoretical time-dependents current permeation showing in Fig.1 are consistent with numerous experimental observation. For example, the permeation transients with typical maxima are found by Iino (1982b), Bockris and Subramanyan (1971). Smooth S-form  $I(\tau)$  dependences are observed by Turnbull et al. (1989), Pyun Su-Il and Oriani (1989).

Small  $\mu$ , when the release rate of hydrogen from traps is small (Fig.1a). At long time, when  $\tau \rightarrow \infty$ , during the calculation with equation (7) the contribution of sum (8)-(10) is very small. Hence, formula (7) can be represented as

$$\ln [I(\tau) - I(\infty)] = \ln [\lambda / (\lambda + \mu)] - (\lambda + \mu)\tau \quad (13)$$

It is shown the creating plot in  $\ln [I(\tau)/I(\infty) - 1]$  versus  $t$  coordinate enable to receive the method for the determination  $\lambda$  and  $\mu$  parameters. The curves founded with the formula (13) for the small  $\mu$  and various  $\lambda$  are shown in Fig.1a by dotted lines. It is necessary to mark that the calculations for common equation of current permeation (7) are consistent with calculations with approximation (13) during decay transient after maximum up to steady state. With the decreasing  $\lambda$  the region of capacity for work is increased.

Large  $\mu$ , when the release rate of hydrogen from traps is large (Fig.1b). For the  $\tau \rightarrow \infty$  and large  $\mu$  from equation (7) can be received

$$\ln [1 - i(t)/i'(\infty)] = \ln 2 - \pi^2 D_{tr} t / L^2 \quad (14)$$

where  $i'(\infty) = nFD_{tr}C_H^0/L$ ;  $D_{tr} = D_H\mu/(\lambda + \mu)$ . The calculations with formula (14) are shown in Fig.1b by dotted lines. It is observed the good coincidence with curves of common equation during the shifting of curve to the steady state. With the decreasing  $\lambda$  the region of capacity for work is increased, as for small  $\mu$ .

For the average  $\mu$  (Fig.1c) the region of capacity for work of approximations (13) and (14) is very small. However, existence in this case two approximate equations enable to estimate the  $\lambda$  and  $\mu$  values by the numerical calculations.

Thus, the using of the approximate equations (13), (14) enable to obtain the constants of hydrogen interaction with metal defects. But for the estimation of  $k_1$  and  $k_2$  it is necessary to determine the lattice diffusion coefficient of hydrogen  $D_H$  and hydrogen concentration at entry of membrane  $C_H^0$ .

## EXPERIMENTAL METHOD

Hydrogen permeation experiments were conducted by the electrochemical method (Devanathan and Stachurski, 1962). The cathode chamber contained the acid electrolyte (0,1 M  $H_2SO_4$  with 4 mg/l  $H_2SeO_4$  added as a hydrogenation promoter), and anode chamber - 0,1 M KOH aqueous solution. For membranes was used the thin steel, 0,5 mm thickness and following chemical composition (%) C - 0,18; Mn - 0,92; Si - 0,34; S - 0,007; P - 0,015; Cr - 1,22; Ni - 0,04. Mechanical properties of the used specimens: ultimate strength - 123  $Kg/mm^2$ , bursting strength - 243 MPa, specific elongation - 5 pct.

## RESULTS AND DISCUSSION

Figure 3 illustrates the dependences of the current permeation versus time for steel with various cathodic current densities. It is shown that the curves have a maximum. The stationary current values increases with the increasing of the current densities. Maximum becomes more obvious and is shifted to the short times. When the hydrogen interaction with metal phase is absence, the permeation kinetic curves does not distinguished from the classical curve. This enable to determine the lattice diffusivity  $D_H$  and hydrogen concentration  $C_H^0$  at the input surface of membrane from plot  $\ln[i(t)t^{1/2}]$  vs  $1/t$ . From the slope of plot is evaluated  $D_H$ , and from segment, which cutting off it on axis  $\ln[i(t)t^{1/2}] - C_H^0$ .

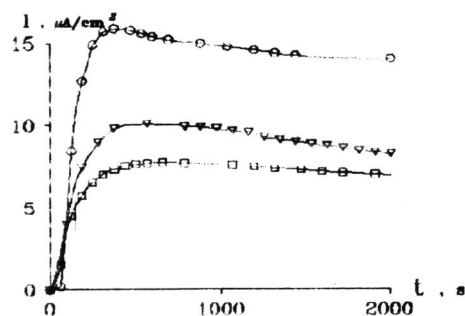


Fig.3. Dependences the current permeation versus time for steel 65ΓX for various current polarization values:  $\square$  -  $I=100$  mA;  $\nabla$  -  $I=150$  mA;  $\circ$  -  $I=370$  mA

Results of calculations with the developed mathematical model are given in Table. From table it is shown that the increasing of the current density tends to increasing of parameter  $\mu$  and does not influenced on  $\lambda$ .

Table  
The kinetic parameters of the diffusion and hydrogen interaction with traps in steel.

Polarization current, mA	$D_H \times 10^{10}$ , $cm^2/s$	$C_H^0 \times 10^{10}$ , mol/cm <sup>3</sup>	Calculated		$Nk_1 \times 10^{10}$ , s <sup>-1</sup>	$k_2 \times 10^{10}$ , s <sup>-1</sup>
			$\lambda$	$\mu$		
100	2.38	1.74	0.2	0.15	1.9	0.95
150	2.31	2.34	0.22	0.22	2.77	1.85
370	2.82	3.08	0.25	0.48	2.82	5.08

Similar  $\lambda/\mu$  ratio and values  $Nk_1$  and  $k_2$  determined for iron alloys with more simplified model was obtained by Pressouyre and Bernstein (1978).

Thus, the parameters of the hydrogen interaction with metal phase,  $\lambda$  and  $\mu$ , obtained by the various methods, enable with the calculations of general equation for current permeation, to compare the shape of the theoretical dependence  $I(\tau)$  with experimental.

This is shown in Figure 5, where illustrates in non-dimensional form the experimental data (Fig. 3 (points)) and theoretical dependence  $I(\tau)$ , calculated with general equation (7). The values  $D_H$  and  $C_H^0$ , obtained from approximation

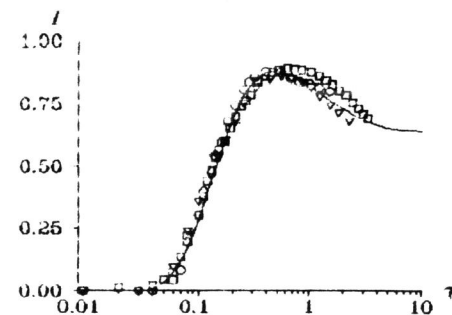


Fig.5. The time-dependents of the current permeation for the steel 65ΓX in non-dimensional form. (—) - theory for  $\lambda=0.25$  and  $\mu=0.45$ .  $\square$  -  $I=100$  mA;  $\nabla$  -  $I=150$  mA;  $\circ$  -  $I=370$  mA (experimental data)

at short time, is used for the transfer of experimental results to non-dimensional form. As shown from Figure 5, the

majority of experimental points are in accord with theoretical dependence, and this fact we consider as one of the arguments of the capacity for work of generalized model of the hydrogen interaction with reversible traps in metal.

#### CONCLUSION

It should be noted that elaborated by us the generalized model considerable extends the experimental possibility of the electrochemical hydrogen permeation technique. The developed theory enable to determine the constants of the hydrogen interaction processes with metal phase from the experimental data.

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