DIFFUSION AND PERMEATION COEFFICIENTS OF HYDROGEN IN NITROGEN ALLOYED STEELS

J. GEORGIEV, CH. MALTSEV, IV. JORDANOVA, IL. PECHENJAKOV, R. DOBREV*

The diffusion and permeation coefficients of hydrogen in nitrogen alloyed steels in temperature range 353-723K are investigated using a mass-spectrometry method. The activation energy of the processes are estimated.

INTRODUCTION

Metal-hydrogen systems have a large practical significance as almost all modern tendencies of the power industry are connected with their application. For the nuclear energetics it is important to create a special class of construction materials, stable enough at different conditions, to construct thermally stable delay elements, to select materials for the first wall of the fusion reactors. For the hydrogen power industry itself very important are the materials for absorption, transportation and desorption of hydrogen.

THEORY

For the estimation of the diffusion coefficient of hydrogen in metals and alloys, it is necessary to solve the differential equation $\partial C/\partial t = D\partial^2 C/\partial x^2$ at non-steady state. The solution of this equation gives (1) :

$t_{lag} = L^2/6D$ . . . . (1)

where t_{lag} is time lag that can be estimated from the equation

$F_0 = F(t_{lag}) = 0.6293F_s$ . . . . . (2)

The coefficient of diffusion can be calculated from (1) and according to following expressions (2):

$D_{b\text{-}t} = 0.4985L^2/\pi^2 t_{b\text{-}t}$ . . . . (3)

$D_{inf} = 0.9242L^2/\pi^2 t_{inf}$ . . . . (4)

where, $t_{b\text{-}t}$ is time, corresponding to the hydrogen penetration and t_{inf} is the

* Institute of Metal Science and Technology (IMST) of Bulgarian Academy of Sciences

time, corresponding to the inflection point.(2)

APPARATUS

The used apparatus has been described in details in a previous paper (3). The apparatus is connected with a Apple II compatible computer, which operates automatically with the MI-1201B system. A computer program is created to control the apparatus. In Fig.1 a typical curve of hydrogen permeation through steel (38XH3MAΦA), is shown. From it by the equations (1,3,4) the corresponding values of the coefficient of diffusion of hydrogen are estimated. The small differences between these values confirm the reliability of the measurements.

DESCRIPTION OF THE METHOD

The membrane with defined working area and thickness (see Fig. 2) is inserted between the flanges of the diffusion cell and after the limiting vacuum ($4\text{-}5 \times 10^{-7}$ Pa) is reached, the heating system is switched on. A preliminary thermal treatment of the assembly at temperature with about 100K higher that the used for the measurements is obligatory. After reaching the working temperature, pure hydrogen with proper pressure is introduced into the entrance chamber of the diffusion cell. By the mass-spectrometer the gas flux through membrane as a function of time is observed. After the steady state has been reached, the hydrogen is pumped out from the entrance chamber. This cycle has been carried out at several different hydrogen pressures.

For the quantive estimation of the hydrogen permeability it is necessary to calibrate the mass-spectrometer, i.e. to obtain a dependence of the ion current - U on the quantity of introduced in the ion source gas per unit time - G, U = f(G)

From the values of the steady state flux permeating through the membrane and from the calibrating curve, the permeability can be estimated.

RESULTS AND DISCUSSION

Specimens made of steels X17AΓ14, X18AΓ20, X18AΓ20Φ, 12X18H9T and 38XH3MAΦA have been investigated and compared with the 12X18H10T. (4)

TABLE 1 - Chemical composition of the investigated steels

STEEL	Cr	Mn	N	Si	C	V	Ni	Mo	Ti
X18AΓ20	18.51	20.88	0.71	0.53	0.09				
X18AΓ20Φ	17.50	19.66	0.75	0.51	0.09	1.1			
X17AΓ14	16.40	13.50	0.33	0.17	0.05				
38XH3MAΦA	1.49	0.28	0.08	0.14	0.26	0.16	3.37	0.34	
12X18H9T	18	≤2		≤0.8	≤0.12		8.5	≤0.3	≤0.5

Membranes of the investigated steels with a defined thickness and working area were made. To prevent the surface influence on the diffusion processes, the input side of the membrane (high pressure side) where the hydrogen pressure is 10^{3}-10^{5} Pa, was coated with a thin layer of vacuum evaporated palladium. The surface activation of the membrane with highly permeable palladium does not change its permeability(5).

The obtained results for the coefficients of diffusion - D and permeation - P are represented as Arrhenius plots in Fig.3 and 4. From this plots the pre-exponential terms and activation energies of the processes are estimated. The results are shown in table 2.

TABLE 2 Pre-exponential Terms and Activating Energies

Material	Permeability $mol/ms\sqrt{Pa}$	Permeability kJ/mol	Diffusivity m^2/sec	Diffusivity kJ/mol
X18AГ20	5.05×10^{-8}	53.15	1.63×10^{-7}	42.56
X18AГ20Ф	3.82×10^{-8}	57.34	3.90×10^{-6}	61.79
X17AГ14	3.16×10^{-7}	64.40	1.18×10^{-6}	54.05
38XH3MAФA	2.75×10^{-7}	33.50	4.87×10^{-8}	12.20
12X18H9T	4.64×10^{-7}	67.30	9.54×10^{-7}	50.90
12X18H10T *		72.49	8.60×10^{-7}	50.20
304SS**	6.25×10^{-7}	65.40	8.25×10^{-7}	49.70

* - ref. (4) ** - ref. (6)

SUMMARY

A method, based on the data taken by a mass-spectrometer, for investigation of the permeability of hydrogen through metals and alloys has been created. Using this method the permeability of hydrogen through nitrogen alloyed steels has been investigated. The coefficients of diffusion of hydrogen in the temperature range 353-723K are obtained, which completes the service characteristics of the designed in the IMST new types of construction steels.

REFERENCES

1. La diffusion dans les solides par Adda Y. et Philibert J., tome I. Presses universitaires de France, 1966

2. Ewald Wicke, Franz Verfuss and Arno Siegmar Schimdt, Z. Metallkunde, Bd. 74 (1983) H.1 p. 7-11.

3. Георгиев Й., Димова В., Печеняков И., Ячков Н., Гюров С. - Научна сесия 88 „Нови материали и технологиив машиностроенето", Русе, окт.1988 г.

4. Арчаков И., Водородная коррозия стали, М. Металлургия, 1985

5. Schenck H., Taxhet H., Diffusion und Durchgang von Wasserstof bei reinem Eisen und bei Stahl im Bereih hoherer Temperaturen, Archiv fur das Eisenhuttenwessen, 1959, v. 30, № 11, p. 661-671.

6. Tanabe T., Yamanishi Y., Sawada K. and Imoto S. , Hydrogen transport in stainless steels, J. Nucl. Mater., 122 and 123, 1984, p. 1568-1572

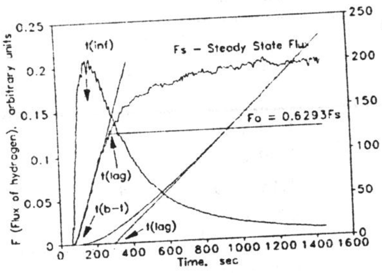

Figure 1 Typical curve of hydrogen permeation through steel 38XH3MAΦA; T = 513K; P = 12,6 kPa; L = 3.10^{-3}m; S = $3,14.10^{-4}$ m^2

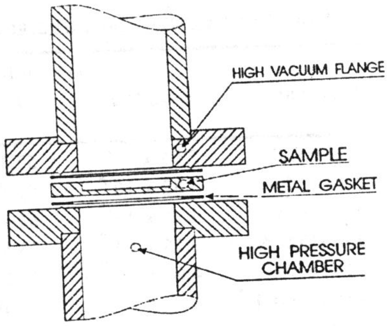

Figure 2 Scheme of the gasket-seal assembly used for hydrogen permeation studies

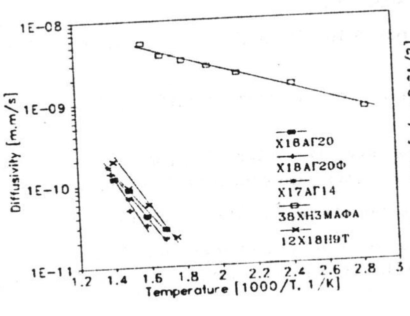

Figure 3 Arrhenius plots for hydrogen diffusivity in various steels

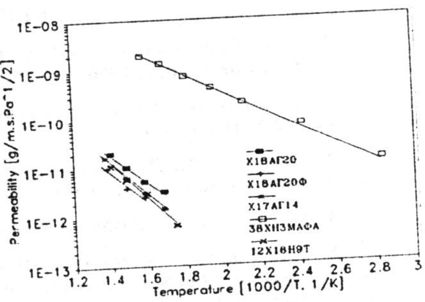

Figure 4 Arrhenius plots for hydrogen permeability through various steels