DIFFUSION AND PERMEATION COEFFICIENTS OF HYDROGEN IN NITROGEN ALLOYED STEELS

J. GEORGIJEV, 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):

\[ t_{lag} = L^2 / 6D \]

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

\[ F_0 = F \left( t_{lag} \right) = 0.6293Fs \]

(2)

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

\[ D_{ht} = 0.4985L^2/2t_{ht} \]

(3)

\[ D_{inf} = 0.9242L^2/2t_{inf} \]

(4)

where, \( t_{ht} \) is time, corresponding to the hydrogen penetration and \( t_{inf} \) is the

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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 (38XH3MAΦА), 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 (4.5x10^-7 Pa) is reached, the heating system is switched on. A preliminary thermal treatment of the assembly at temperature with about 100 K 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 X17Аγ14, X18Аγ20, X18Аγ20Φ, 12X18H9T and 38XH3MAΦА have been investigated and compared with the 12X18H10T. (4)

<table>
<thead>
<tr>
<th>STEEL</th>
<th>Cr</th>
<th>Mn</th>
<th>N</th>
<th>Si</th>
<th>C</th>
<th>V</th>
<th>Ni</th>
<th>Mo</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>X18Аγ20</td>
<td>0.18</td>
<td>0.28</td>
<td>0.71</td>
<td>0.53</td>
<td>0.09</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>X18Аγ20Φ</td>
<td>0.17</td>
<td>0.25</td>
<td>0.75</td>
<td>0.51</td>
<td>0.09</td>
<td>1.1</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>X17Аγ14</td>
<td>0.16</td>
<td>0.33</td>
<td>0.33</td>
<td>0.17</td>
<td>0.05</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>38XH3MAΦА</td>
<td>0.14</td>
<td>0.26</td>
<td>0.16</td>
<td>0.37</td>
<td>0.34</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12X18H9T</td>
<td>0.18</td>
<td>≤0.2</td>
<td>≤0.8</td>
<td>≤0.12</td>
<td>8.5</td>
<td>≤0.3</td>
<td>≤0.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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^-7 Pa, was coated with a thin layer of vacuum evaporated palladium. The surface activation of the membrane with highly permeable palladium does not change.

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its permeability.

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

<table>
<thead>
<tr>
<th>Material</th>
<th>Permeability</th>
<th>Diffusivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mol/m² Pa⁻¹</td>
<td>m²/sec</td>
</tr>
<tr>
<td>X18A120</td>
<td>5.05 x 10⁻⁵</td>
<td>1.63 x 10⁻⁷</td>
</tr>
<tr>
<td>X18A120F</td>
<td>3.82 x 10⁻⁸</td>
<td>3.90 x 10⁻⁶</td>
</tr>
<tr>
<td>X17A14</td>
<td>3.16 x 10⁻⁷</td>
<td>1.18 x 10⁻⁵</td>
</tr>
<tr>
<td>38XH3MAFA</td>
<td>2.75 x 10⁻⁷</td>
<td>4.87 x 10⁻⁸</td>
</tr>
<tr>
<td>12X18H9T</td>
<td>4.64 x 10⁻⁷</td>
<td>9.54 x 10⁻⁷</td>
</tr>
<tr>
<td>12X18H10T</td>
<td>7.24 x 10⁻⁸</td>
<td>8.60 x 10⁻⁷</td>
</tr>
<tr>
<td>304SS</td>
<td>6.25 x 10⁻⁷</td>
<td>8.25 x 10⁻⁷</td>
</tr>
</tbody>
</table>

* - 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
4. Archanov I., Водородна коррозия стали, М. Металлургия, 1985
Figure 1 Typical curve of hydrogen permeation through steel 38XH3MAФА; 
\( T = 513K ; \ P = 12.6 \text{ kPa} ; \ L = 3.10^{8} \text{m} ; \\
S = 3.14.10^{4} \text{ 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

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