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Heavy hydrogen isotopes penetration through austenitic and martensitic steels

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Abstract

Experimental results are presented of deuterium and tritium permeability through samples of nickel, austenitic steel (16Cr–15Ni–3Mo–Ti), and martensitic steel DIN 1.4914 (MANET) exposed to a gaseous phase. Experiments were carried out at the RFNC–VNHTF installation, which has the capability of measuring the permeability of hydrogen isotopes by mass spectrometry over a temperature range of 293–1000 K, hydrogen isotope pressure ranges of 50–1000 Pa. Sample disks (30 and 40 mm diam.) can be assembled in the test chamber by electron-beam welding or mounted (30-mm diam. disks) on gaskets. Diffusion and permeability dependencies on temperature and pressure are determined and corresponding activation energies are presented.

1. Introduction

The interaction of tritium with fusion reactor structural materials is of great importance for safety considerations, because of the high probability of tritium permeation through the materials during high-temperature reactor operation. Determining the parameters of the interaction between heavy hydrogen isotopes and various metals, including diffusion, solubility, and permeation of tritium through structural materials, is essential to accurately calculate recycling, outgassing, loading, permeation, and hydrogen embrittlement.

Investigations of permeation of heavy hydrogen isotopes through fusion reactor candidate materials were carried out at the special experimental installation in the tritium laboratory at RFNC–VNIITF.

Various parameters of gas–metal interactions were determined by measuring hydrogen permeation. Parameters specific to the kinetics of permeation of hydrogen isotopes through metal membranes, in a wide range of temperatures and pressures, were obtained.

Because the permeation and diffusion of hydrogen and deuterium in nickel have been studied extensively [1,2], experiments using nickel membranes were carried out to calibrate the apparatus. Then, studies were undertaken using deuterium and tritium to investigate their interaction with various materials of interest for use in fusion reactor structural components, including austenitic dispersion-hardened steel 16Cr–15Ni–3Mo–Ti and martensitic steel DIN 1.4914 (MANET).

2. Description of experiment

2.1. Theoretical background of the experiments

To investigate the permeation of heavy hydrogen through candidate materials, a dynamic technique to maintain a constant flux was developed. This method ensures sufficient accuracy and purity of the experiment and allows information to be obtained concerning parameters specific to the permeation of hydrogen isotopes through metal membranes.

Parameters of diffusion and permeation were calculated based on a model that describes the process of permeation limited by diffusion.

Permeation factor P was calculated from the expression for fixed flux J_{st},

$$J_{st} = P\frac{S}{I}\left(p_1^{1/2} - p_0^{1/2}\right), \tag{1}$$

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where S is the area of the membrane's surface, l the thickness of the membrane, and p_1, p_0 are the gas pressures on the inlet and outlet membrane surfaces, respectively. For experimental conditions, where ($p_0 \ll p_1$), the value p_0 may be ignored.

Diffusion factor D was determined from the kinetic curves of the permeating flux by the 'time-lag' method. Time-lag τ corresponds to the time point on the kinetic curve when the flux equals $0.63J_{st}$:

$$D = \frac{l^2}{6\tau}. \tag{2}$$

In terms of the classical mechanism of diffusion, it is proposed that the medium does not affect the diffusing substance. In this case, temperature dependencies of diffusion and permeation factors are described by the Arrhenius equations:

$$\begin{aligned} D &= D_0 \exp(-E_d/RT), \\ P &= P_0 \exp(-E_p/RT), \end{aligned} \tag{3}$$

where D_0 and P_0 are pre-exponent factors, E_d and E_p are activation energies for diffusion and permeation, respectively, R the universal gas constant, and T is temperature.

2.2. Apparatus and procedure

A diagram of the experimental apparatus for investigating the permeation of heavy hydrogen isotopes metal membranes is shown in Fig. 1. The installation is based on two vacuum chambers, K1 and K2, separated by a membrane of the material being investigated. Assembling and sealing of the membrane may be accomplished in two ways: by electron-beam welding of the austenitic steel samples to the stainless steel girdle (ensures sealing of samples having a diameter $\leqslant$40 mm); or by use of a flange connection, with sealing of the martensitic steel sample by gold gaskets (ensures sealing of disks with diameter 40 or 30 mm).

Chamber K1 serves for tritium input through the valve VH01. The purification system is based on a palladium Pd filter and is used to prepare the hydrogen before the experiment. Chamber K2 is supplied by omegatron gauge S2, which measures the deuterium or tritium flux permeated through the sample. The sample is heated by an electric heater. A specially designed control system connected to the membrane-sealing unit automatically adjusts the heater to maintain the desired temperature. All parameters of the installation are regulated, treated and stored in a controlling computer. During the experiment, the following parameters are measured: sample temperature, hydrogen pressure over membrane inlet surface, and the elapsed time, amount, and fixed flux of tritium permeated through the sample.

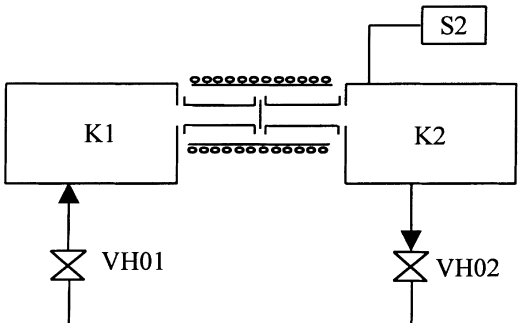

Fig. 1. Scheme of the installation.

3. Results and discussion

3.1. Permeation of heavy hydrogen isotopes through nickel

Permeation experiments through nickel having a 99.985 wt% Ni were carried out in a temperature range of 550–1030 K and hydrogen isotope pressures over the membrane inlet side of 40–1350 Pa.

Permeating flux measurements at different hydrogen pressures over the membrane inlet side showed a diffusion limited permeation dependence of $J_{st} \sim \sqrt{p}$. Diffusion and permeation factors for each temperature of the experiment was determined using Eqs. (1) and (2). All obtained dependencies are described by the following Arrhenius equations.

For the Ni–D_2 system:

$$^{Ni}D_D = 3.8 \times 10^{-7} \exp(-38/RT)\ (m^2/s),$$

$$^{Ni}P_D = 6.0 \times 10^{-7} \exp(-59/RT)\ (mol/m\ s\ Pa^{1/2}).$$

For the Ni–T_2 system:

$$^{Ni}D_T = 2.3 \times 10^{-7} \exp(-36/RT)\ (m^2/s),$$

$$^{Ni}P_T = 7.4 \times 10^{-8} \exp(-49/RT)\ (mol/m\ s\ Pa^{1/2}).$$

Activation energies are given in kJ/mol.

The ratio of values $^{Ni}D_D$ and $^{Ni}D_T$ for the temperature range investigated in these experiments is between 1.11 and 1.35. This is in good agreement with theory, which predicts

$$\frac{^{Ni}D_D}{^{Ni}D_T} = \sqrt{\frac{m_T}{m_D}} = 1.22,$$

where m_D and m_T are the masses of the deuterium and tritium atoms, respectively. Comparison of the experimental data with measurements of other investigators [1] shows agreement within limits of 20–30%.

3.2. Deuterium and tritium permeation through dispersion-hardened steel 16Cr–15Ni–3Mo–Ti

Investigations of deuterium and tritium permeation through austenitic steel 16Cr–15Ni–3Mo–Ti were carried out in a temperature range of 760–1090 K at hydrogen pressures over the membrane inlet surface of 1.5×10^2 to 4.0×10^4 Pa. A series of kinetic curves $J = J(t)$ was obtained in the pressure range 150–500 Pa at several different temperatures. The relationship $J_{st}/\sqrt{p} = f(p)$ was determined. Deuterium permeation through steel in the temperature range 465–813 K and pressure range 150–500 Pa is described by the function $J_{st} \sim p^z$, where z is in the range 0.50–0.67. Such dependence on pressure corresponds to a diffusion-limited permeation regime. The deviation from $\sim\sqrt{p}$ is connected with the presence of an oxide film on the sample surface [3], which may be formed during vacuum annealing of the sample. Experiments to determine permeation factors and effective factors of diffusion were carried out for deuterium and tritium 96 mol% $T_2 + 4$ mol% D_2 with total content of impurities of less than 10^{-4} mol%. Results are shown in Figs. 2 and 3.

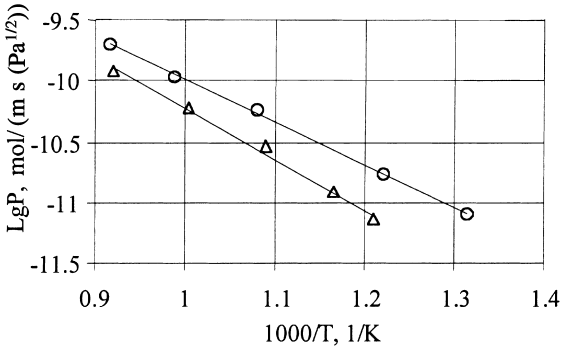

Fig. 2. Temperature dependencies of permeation factors through steel 16Cr–15Ni–3Mo–Ti: (○) deuterium; (△) tritium.

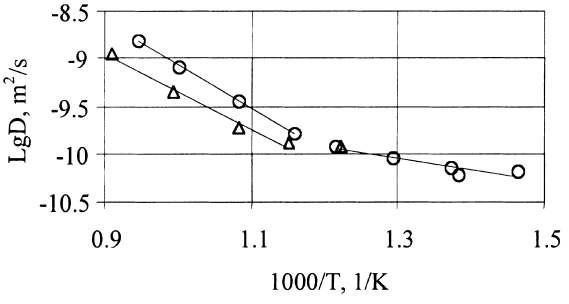

Fig. 3. Diffusion in steel 16Cr–15Ni–3Mo–1Ti. (○) Deuterium; (△) Tritium.

The temperature dependencies of permeation and diffusion factors (850–1090 K) for tritium obtained were as follows:

$$^{A}P_T = 9.2 \times 10^{-7} \exp(-80/RT) \text{ (mol/m s Pa}^{1/2}\text{)},$$
$$^{A}D_T = 1.2 \times 10^{-5} \exp(-85/\mathrm{RT}) \text{ (m}^2\text{/s)}.$$

The deviation of the temperature dependencies of diffusion factors from Arrhenius's law and the discrepancy between the classic value of mass relation with the obtained ratio for diffusion factors may be caused by trapping of the diffusing substance. The presence of traps is confirmed by the effective diffusion factor dependence on gas pressure over the inlet side and by the results of residual tritium distribution experiments in 16Cr–15Ni–3Mo–Ti steel by microautoradiography [4].

It should be noted that a specific feature of the steel investigated in this experiment is the presence of the dispersed hardening phase of Ni3Ti, which causes structural instability of the membrane material during dissolving in matrix at temperatures of ~850 K and higher. This, in turn, affects the diffusion factor.

3.3. Permeation of heavy hydrogen isotopes through martensitic steel DIN 1.4914 (MANET)

Investigations of the permeation of heavy hydrogen isotopes through martensitic steel MANET were carried out in a temperature range of 520–900 K at gas pressures over the inlet membrane side of 4×10^2 to 5.6×10^4 Pa. Experimental results are shown in Figs. 4 and 5.

The dependence of permeation on temperature is described by Arrhenius plots and are shown in Fig. 4. The good agreement of values obtained for these experiments with those shown in [5] for tritium with 'virgin' steel should be noted.

Diffusion factors were determined by calculating kinetic curves of permeation and are shown in Fig. 5. The

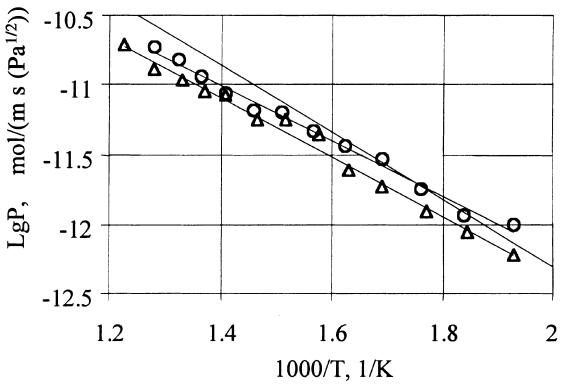

Fig. 4. Temperature dependencies of permeation factors through MANET: (○) deuterium; (△) tritium (–) Tritium in virgin steel [6].

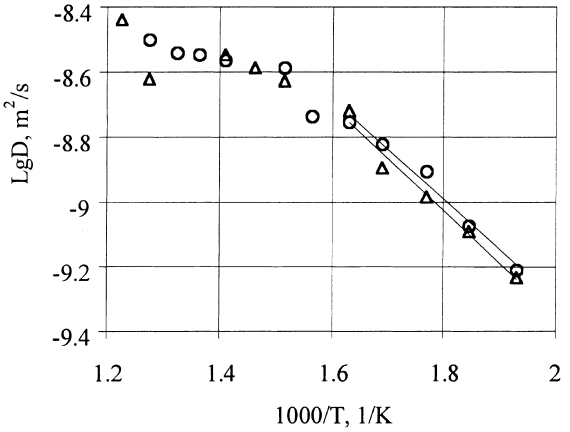

Fig. 5. Diffusion in MANET: (○) deuterium; (△) tritium.

relative error in determining diffusion factors and permeation factors appearing as a result of variations in the dimensions of the samples and the physical parameters of the experiments is the same as that for the case of nickel.

Plots of temperature dependencies of diffusion and permeation factors are described by the following Arrhenius equations.

For MANET–D_2 system:

$$^{M}D_D = 6.6 \times 10^{-7} \exp(-29/RT)\ (m^2/s),$$

$$^{M}P_D = 6.1 \times 10^{-9} \exp(-39/RT)\ (mol/m\ s\ Pa^{1/2}).$$

For MANET–T_2 system:

$$^{M}D_T = 5.0 \times 10^{-7} \exp(-29/RT)\ (m^2/s),$$

$$^{M}P_T = 7.7 \times 10^{-9} \exp(-41/RT)\ (mol/m\ s\ Pa^{1/2})$$

Activation energies are expressed in kJ/mol.

Expressions for diffusion factors are shown for a temperature range of 520–620 K. The ratio of values of $-D_D$ and $-D_T$ in this temperature range is in good agreement with theory and is equal to 1.18. The increase in diffusion energy in the low-temperature range (Fig. 4) is probably connected to the presence of an oxide layer on the membrane surface [5,6], because the effect of this process increase as temperature declines. The formation of new phases (admixtures) on grain boundaries may be sufficient to cause the reduction of diffusion.

4. Conclusions

In the given temperature range, the permeation of heavy hydrogen isotopes through austenitic steel 16Cr–15Ni–3Mo–1Til and martensitic steel DIN 1.4914 (MANET) was shown to be limited by diffusion of deuterium and tritium atoms. From kinetic curves of permeation, parameters of permeation and diffusion were calculated:

$$^{A}D_T = 1.2 \times 10^{-5} \exp(-85/RT)\ (m^2/s),$$

$$^{M}D_T = 5.0 \times 10^{-7} \exp(-29/RT)\ (m^2/s),$$

$$^{A}P_T = 9.2 \times 10^{-7} \exp(-80/RT)\ (mol/m\ s\ Pa^{1/2}),$$

$$^{M}P_T = 7.7 \times 10^{-9} \exp(-41/RT)\ (mol/m\ s\ Pa^{1/2}).$$

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