Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Journal of Nuclear Materials 326 (2004) 47–58
journal of nuclear materials
www.elsevier.com/locate/jnucmat

Permeability of hydrogen and deuterium of Hastelloy XR

Tetsuaki Takeda [a,*], Jin Iwatsuki [b], Yoshiyuki Inagaki [a]

[a] *Department of Advanced Nuclear Heat, Japan Atomic Energy Research Institute, Oarai-machi, Higashi-ibaraki-gun, Ibaraki-ken 311-1394, Japan*
[b] *Energy System Division, Ishikawajima-Harima Heavy Industries Co. Ltd., Shin-nakahara-cho, Isogo-ku, Yokohama 235, Japan*

Received 5 November 2002; accepted 26 December 2003

Abstract

Permeation of hydrogen isotope through a high-temperature alloy used as heat exchanger and steam reformer pipes is an important problem in the hydrogen production system connected to be a high-temperature engineering test reactor (HTTR). An experiment of hydrogen (H_2) and deuterium (D_2) permeation was performed to obtain permeability of H_2 and D_2 of Hastelloy XR, which is adopted as heat transfer pipe of an intermediate heat exchanger of the HTTR. Permeability of H_2 and D_2 of Hastelloy XR were obtained as follows. The activation energy E_0 and pre-exponential factor F_0 of the permeability of H_2 were $E_0 = 67.2 \pm 1.2$ kJ mol^{-1} and $F_0 = (1.0 \pm 0.2) \times 10^{-8}$ m^3(STP) m^{-1} s^{-1} Pa$^{-0.5}$, respectively, in the pipe temperature ranging from 843 K (570 °C) to 1093 K (820 °C). E_0 and F_0 of the permeability of D_2 were respectively $E_0 = 76.6 \pm 0.5$ kJ mol^{-1} and $F_0 = (2.5 \pm 0.3) \times 10^{-8}$ m^3(STP) m^{-1} s^{-1} Pa$^{-0.5}$ in the pipe temperature ranging from 943 K (670 °C) to 1093 K (820 °C).

PACS: 66.30; 68.45.D; 64.75

1. Introduction

The full power operation (30 MW) of the high-temperature engineering test reactor (HTTR) [1], which is the first high-temperature gas-cooled reactor (HTGR) in Japan, was achieved in December 2001 at JAERI. After the reactor performance and safety demonstration test will be performed for several years, a hydrogen production system [2] by steam reforming of natural gas (HTTR hydrogen production system) will be connected with the HTTR. Prior to coupling of the steam reforming system with the HTTR, an out-of-pile test [3] and design study are performed to confirm the controllability, operability and safety of this system under simulated operational conditions. In order to obtain detailed data for a safety review and development of numerical analysis codes, an experiment on permeation of hydrogen isotope [4], a corrosion test of a catalyst pipe, and an integrity test of a high-temperature isolation valve are being performed as an essential test in parallel to the out-of-pile test.

Permeation of tritium is an important problem in regard to a release of the radioactive substance from the HTTR hydrogen production system. Fig. 1 shows an outline of tritium and hydrogen transport process in the HTTR hydrogen production system. There are several sources for a production of tritium in the HTTR [5]. In comparison to the other nuclear reactors, the HTTR has graphite components containing lithium as impurity in the reactor and its coolant gas helium has He-3 isotope, which produces tritium. The inventories of these sources have their maximum in the initial period of reactor operation and consequently due to burning up the amount of these nucleates decreases during reactor

---

[*] Corresponding author. Tel.: +81-29 264 8707; fax: +81-29 264 8710.
E-mail address: takeda@popsvr.tokai.jaeri.go.jp (T. Takeda).

0022-3115/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2003.12.011

Nomenclature

C	molar concentration [–]
d_i	inner diameter of pipe
d_t	thickness of pipe
D	diffusivity [$m^2\,s^{-1}$]
E_0	activation energy [$kJ\,mol^{-1}$]
F_0	pre-exponential factor [$m^3(STP)\,m^{-1}\,s^{-1}\,Pa^{-0.5}$]
J	steady-state permeation flux [$m^3(STP)\,m^{-2}\,s^{-1}$]
K_p	permeability [$m^3(STP)\,m^{-1}\,s^{-1}\,Pa^{-0.5}$]
l, L	length of the test and measurement pipe [m]
p_i	hydrogen partial pressure in the test pipe [Pa]
p_o	hydrogen partial pressure in the annular passage [Pa]
p_a	hydrogen partial pressure in the outside of the measurement pipe [Pa]
Q	amount of permeated hydrogen [$m^3(STP)\,s^{-1}$]
Q_o	amount of permeated hydrogen through the measurement pipe [$m^3(STP)\,s^{-1}$]
Q_e	amount of permeated hydrogen obtained by the experiment [$m^3(STP)\,s^{-1}$]
R	gas constant [$J\,mol^{-1}\,K^{-1}$]
r, r'	radius of test and measurement pipe [m]
S	solubility [$m^3(STP)\,m^{-3}\,Pa^{-0.5}$]
T	temperature [K]
β	ratio of permeability of hydrogen and deuterium [–]
Subscript	
i	inner
o	outer
f	fluid phase
s	solid phase
H	hydrogen
D	deuterium
XR	Hastelloy XR
X	Hastelloy X

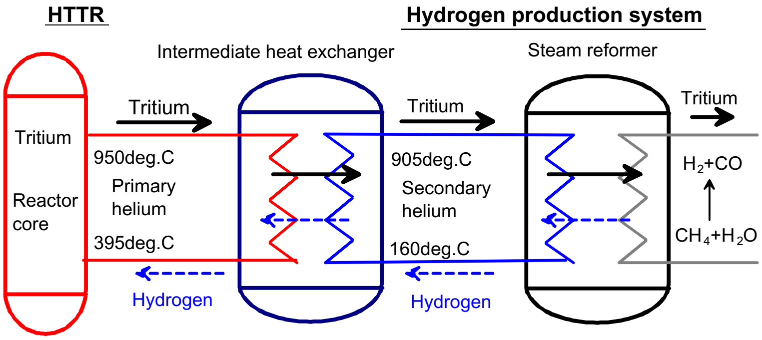

Fig. 1. Tritium and hydrogen transport process in the HTTR hydrogen production system.

operation. Further sources are boron in the control rods and uranium in the fuel particles. Tritium, which produced in the reactor, permeates a heat transfer pipe of an intermediate heat exchanger (IHX) and transfers from a primary cooling system to a secondary cooling system. Finally, it seems to be probable that tritium permeates a catalyst pipe of a steam reformer (SR) and mixes in hydrogen as a product.

On the other hand, hydrogen produced in the SR permeates the catalyst pipe and the heat transfer pipe of the IHX in opposite direction to permeation of tritium. Therefore, it is expected that hydrogen transfers to the primary cooling system and mixes in the helium gas coolant. As hydrogen gets into in the reactor core, a reduction of a purification ability will take place due to rise in the concentration of impurities in the primary cooling system caused by the reaction of the graphite and hydrogen. The primary helium purification system of the HTTR is designed to have hydrogen concentration limited to less than 3 ppm. In order to connect the hydrogen production system with the HTTR, it is necessary to evaluate quantitatively the amount of permeated hydrogen through the IHX and the SR. Hastelloy XR, which is nickel-based alloy, is used as a material of the heat transfer pipe of the IHX, because it is the only material approved as a high-temperature structural material under a high-pressure helium gas condition of the HTTR. In order to take the safety review of the HTTR hydrogen production system, it is necessary to evaluate not only the amount of permeated hydrogen isotope through the IHX but also the amount of tritium mixing in product hydrogen quantitatively. Although it seems to be probable that hydrogen permeability of Hastelloy XR is same as that of Hastelloy X, we could not obtain the real amount of permeated hydrogen isotope in the HTTR hydrogen production system because there were no reports regarding hydrogen permeability of Hastelloy XR. Therefore, it is necessary to obtain permeability of hydrogen isotope through Hastelloy XR tube prior to the construction of the HTTR hydrogen production system.

A permeation rate of hydrogen isotope through a solid metal is an overall rate of transfer of the permeating species from a fluid on one side to the other side. Since this is a serial, multi-step process, the overall rate is governed most strongly by the slowest step in the transport process. According to the previous studies [6–8], the overall permeation rate will depend not only on a hydrogen partial pressure but also on a surface condition of the solid metal. The rate-limiting step for hydrogen permeation is shown in Fig. 2. The permeation process in a comparatively higher hydrogen partial pressure region is mostly governed by diffusion in the solid metal and the amount of permeated hydrogen is in proportion to the difference in square root of the higher side and the lower side of hydrogen partial pressure. The permeation process is governed by chemical adsorption in case of very low hydrogen partial pressure. The amount of permeated hydrogen is in proportion to the difference of the first power of the hydrogen partial pressure in this case. When an oxide film is formed on the surface of the metal, hydrogen diffuses as molecule

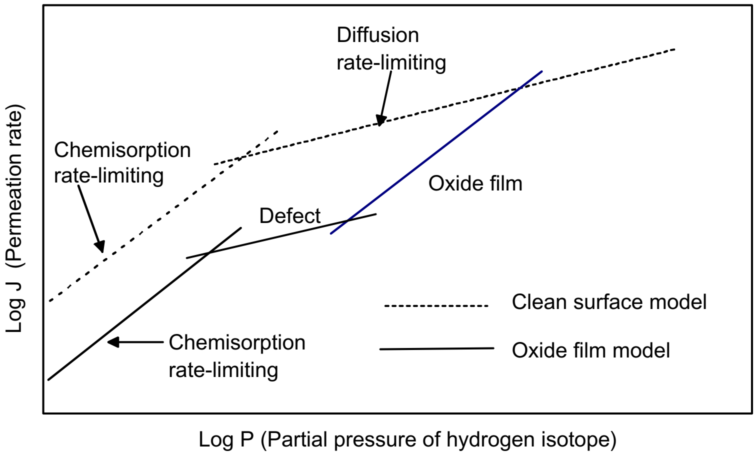

Fig. 2. Rate-limiting step for hydrogen permeation [7].

Table 1
Permeability of hydrogen and deuterium of high-temperature alloys

No.	High-temperature alloy	Pre-exponential factor, K_0 [$m^3(STP)\,m^{-1}\,s^{-1}\,Pa^{-0.5}$]	Activation energy, E_0 [$kJ\,mol^{-1}$]	Temperature, T [°C]	Reference
1	Nickel	7.73×10^{-9}	54.84	–	Robertson [13]
2	Inconel-600	2.22×10^{-8}	66.14	800–1000	Masui et al. [11]
3	Incoloy-600	1.00×10^{-8}	64.05	700–950	Mori and Nakada[a] [10]
4	Incoloy-800	2.13×10^{-8}	69.07	800–1000	Masui et al. [11]
5	Incoloy-800	5.45×10^{-9}	64.05	700–950	Mori and Nakada[a] [10]
6	Incoloy-800	2.31×10^{-8}	74.1	600–950	Rohrig et al. [9]
7	Incoloy-800	9.77×10^{-9}	74.1	649	Strehlow and Savage[b] [6]
8	Hastelloy-N	2.59×10^{-8}	77.99	605	Strehlow and Savage[b] [6]
9	Hastelloy-X	5.62×10^{-9}	58.2	400–600	Namba et al. [12]
10	Hastelloy-X	2.00×10^{-8}	66.98	800–1000	Masui et al. [11]

[a] Some oxide film influence suspected.

[b] For deuterium.

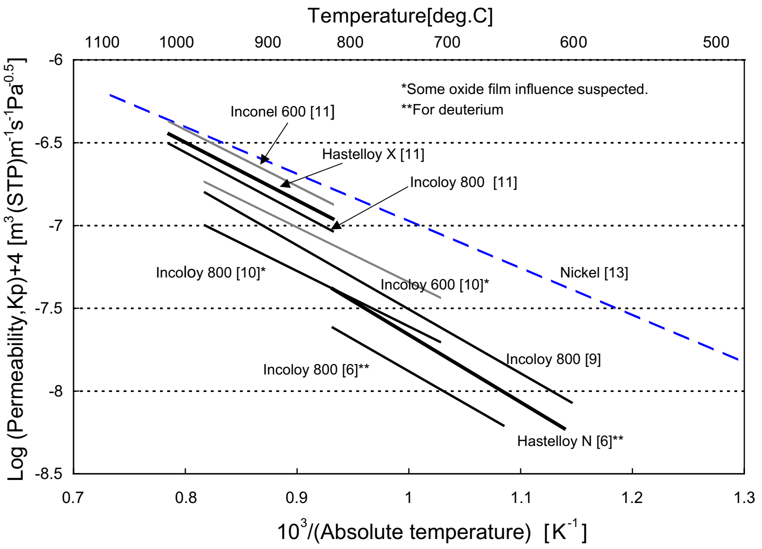

Fig. 3. Permeability of hydrogen and deuterium of high-temperature alloys.

Table 2
Specifications for chemical compositions of Hastelloy XR and X [14]

Material	Chemical compositions (wt%)															
	Range	Elements														
		C	Mn	Si	P	S	Cr	Co	Mo	W	Fe	Ni	B	Al	Ti	Cu
Hastelloy XR	Maximum	0.15	1.0	0.5	0.04	0.03	23.0	2.5	10.0	1.0	20.0	Remainder	0.01	0.05	0.03	0.5
	Minimum	0.05	0.75	0.25	–	–	20.5	–	8.0	0.20	17.0	Remainder	–	–	–	–
Hastelloy X	Maximum	0.15	1.0	1.0	0.04	0.03	23.0	2.5	10.0	1.0	20.0	Remainder	0.01	0.5	0.15	0.5
	Minimum	0.05	–	–	–	–	20.5	0.5	8.0	0.20	17.0	Remainder	–	–	–	–

inside the oxide film because hydrogen molecule adsorbs on the surface without dissociation. The value of the index to the hydrogen partial pressure depends on a state of formation of the oxide film and it takes value inside the range of 1 from 0.5.

A pre-exponential factor and activation energy of permeability of hydrogen and deuterium collected in Arrhenius type are provided in Table 1 and in Fig. 3. There are several reports of permeability of hydrogen and deuterium of a high-temperature alloy such as Incolloy [6,9–11] and Hastelloy [6,11,12]. Hydrogen permeability of HK40, Incolloy 800, Hastelloy X and Inconel 600 in 800–1000 °C was obtained by Masui et al. [11]. They reported that hydrogen permeability of these alloys approaches to that of nickel [13] and activation energy decreases with increasing a nickel content of the alloy. Table 2 shows specifications for chemical compositions of Hastelloy XR and X [14]. Although the chemical composition of Hastelloy XR is similar to that of Hastelloy X, the corrosion resistance of Hastelloy XR is much better in high-temperature helium surroundings. However, there are no reports regarding permeability of hydrogen and deuterium of Hastelloy XR, which is employed not only as a material of the heat transfer pipe of the IHX but also as one of candidate materials of the catalyst pipe of the SR. This paper describes permeability of hydrogen and deuterium of Hastelloy XR and the governing process of the permeation of hydrogen isotope in the HTTR hydrogen production system.

2. Experiments on permeation of hydrogen

2.1. Hydrogen transport process in the HTTR hydrogen production system

Gas pressure inside the catalyst pipe of the SR is about 4.5 MPa in the HTTR hydrogen production system. Then, a hydrogen partial pressure becomes about 2.3 MPa assuming that a mole fraction of hydrogen is 0.5. The hydrogen partial pressure in the primary coolant becomes less than 12 Pa because hydrogen as impurities is limited to less than 3 ppm. Furthermore, the tritium partial pressure is about 3×10^{-4} Pa assuming that tritium exists as HT form [15]. Thus, the pressure range of hydrogen isotope is so wide in the HTTR hydrogen production system.

It is supposed that hydrogen and tritium will exist as molecule from a viewpoint of the dissociation energy of hydrogen molecule in the HTTR hydrogen production system. For example, the required energy to increase the temperature of hydrogen gas of 1 mole from 0 to 1000 °C is about 29 $\mathrm{kJ\,mol^{-1}}$ and the dissociation energy of hydrogen is about 431 $\mathrm{kJ\,mol^{-1}}$. Thus, excitation of molecular by an electromagnetic wave, electrolytic dissociation, and so on are necessary to dissociate hydrogen molecule. The thermal energy in the HTTR hydrogen production system is not really enough to dissociate hydrogen molecule. As far as hydrogen exists as molecule, hydrogen will dissociates and adsorbs on the pipe surface, and then diffuses inside the pipe. Therefore, the amount of permeated hydrogen isotope in the HTTR hydrogen production system is limited by diffusion in the solid metal to be in proportion to the difference in square root of the hydrogen partial pressure, except for the case that the oxide film is formed on the metal surface.

In addition, diffusivity of hydrogen atom in the solid metal is smaller than that of hydrogen molecule in the gas mixture. For instance, diffusivity of hydrogen molecules in helium gas is about $D_{\mathrm{fHe}} = 4.0 \times 10^{-5}\ \mathrm{m^2\,s^{-1}}$ at 1073 K (800 °C) and 4 MPa [16]. On the other hand, diffusivity of hydrogen atom in nickel is about $D_{\mathrm{sNi}} = 6.9 \times 10^{-7} \exp(-4870/T)\ \mathrm{m^2\,s^{-1}}$ in the range of 620–1600 K (347–1327 °C) [17]. As diffusivity in nickel is $D_{\mathrm{sNi}} = 7.37 \times 10^{-9}\ \mathrm{m^2\,s^{-1}}$ at 1073 K, D_{sNi} is about 1.84×10^{-4} of D_{fHe}. Therefore, molecular diffusion in the gas mixture will not become the rate-limiting step of hydrogen transport in the HTTR hydrogen production system.

2.2. Experimental apparatus and procedure

An apparatus is composed of a test section which consists of a permeation test pipe (inside pipe), a measurement pipe (outside pipe), and an electric furnace, a gas supply system, a concentration measurement system, electric instruments, and so on. The partial pressure of hydrogen isotope is measured by a quadrupole mass spectrometer. A schematic drawing of the experimental apparatus is provided in Fig. 4. Table 3 shows the main specification of the apparatus.

According to previous studies, there was a method that an inside of a container was partitioned into two with a metal plate [11,12] and then, hydrogen was poured from one side and permeated hydrogen at the other side was measured. Furthermore, there was a method [6] that hydrogen was poured into the pipe which closed one side and purge gas was flowed into the outside of the pipe and then permeated hydrogen through the pipe was measured. As for the condition of hydrogen partial pressure in this experiment, we have to maintain a constant hydrogen partial pressure in the permeation test pipe. This is because the gas mixture, which contains hydrogen isotope, flows steadily in the

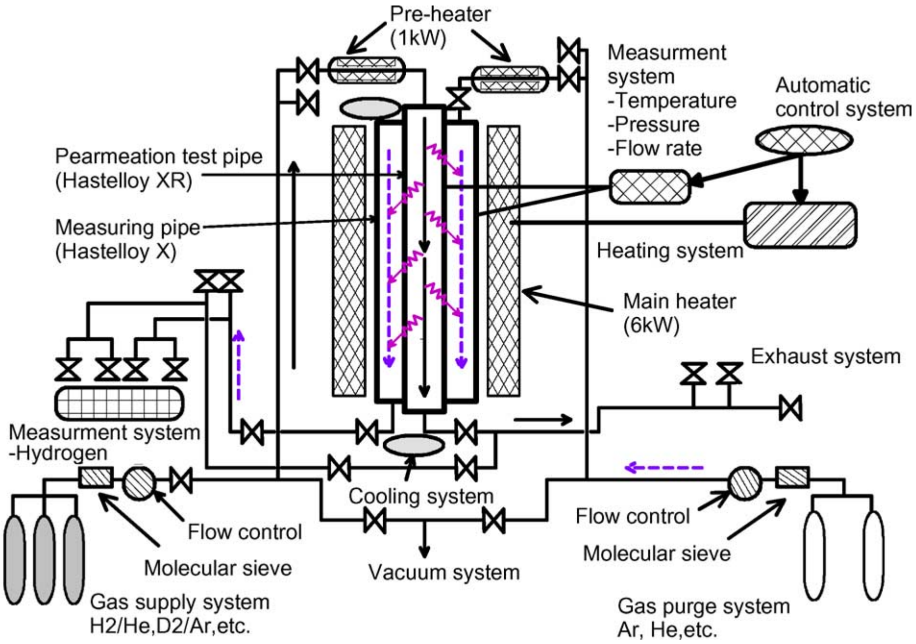

Fig. 4. Experimental apparatus.

Table 3
Main specifications of experimental apparatus

Test section	Coaxial double pipe and electric furnace
Permeation test pipe (inner)	24.8 mm ID, 31.8 mm OD, 3.5 mm thickness, 1000 mm length
Pipe material	Hastelloy XR
Measuring pipe (outer)	50 mm ID, 56 mm OD, 3 mm thickness, 1000 mm length
Pipe material	Hastelloy X
Working fluid	Hydrogen, deuterium, helium, argon, nitrogen
Electric furnace	Main heater 2 kW × 3 regions (vertical direction), pre-heater 1 kW × 2 parts (supply and purge lines)
Maximum temperature	900 °C
Maximum pressure	1 MPa
Flow rate of gas	100 cc(STP)[a] min^{-1}
Hydrogen measurement system	Quadrupole mass spectrometer

[a] Standard condition (0 °C, 0.1 MPa).

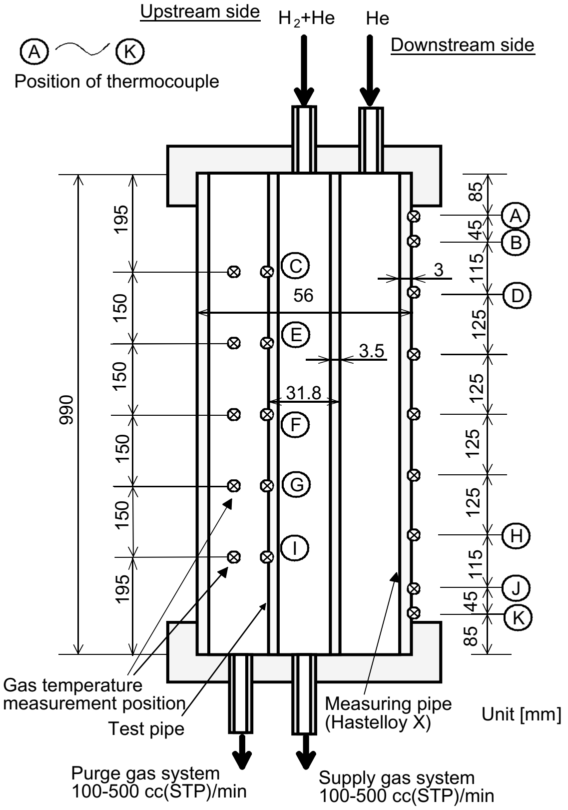

Fig. 5. Test section of apparatus and measured points of wall and gas temperature.

inside and outside of the heat transfer pipe of the IHX and the catalyst pipe of the SR during a normal operation. Therefore, a test section was made a coaxial double pipe structure [18], which inserted the permeation test pipe into the measurement pipe, and gases flowed into the inside and outside of the permeation test pipe under the condition of constant pressure and flow rate. An inside pipe, which is the typical test pipe made of Hastelloy XR, has an inner diameter of 24.8 mm and a thickness of 3.5 mm as it is the same as the dimension of the heat transfer pipe of the IHX. In order to simulate the total pressure of the gas mixture up to 1 MPa, the measurement pipe was made of Hastelloy X whose hydrogen permeability is already known. The outside pipe has an inner diameter of 50 mm and a thickness of 3 mm. The heating area of the electric furnace, which has 6 kW electric powers, is divided into three vertical regions in order to achieve a flat temperature distribution along the pipe. The each part was independently controlled and was heated up to 900 °C. A rough sketch of the test section can be seen in Fig. 5. The heating area between points D through H could be kept a flat temperature. However, the 250 mm regions from the both ends of the pipe were not achieved a flat temperature distribution. A partial pressure of permeated hydrogen decreases with increasing a gas flow rate in an annular passage between the permeation test pipe and the measurement pipe. So, a volumetric flow rate in the annular passage was decided from the result of a preliminary analysis [19]. The control range of the volumetric flow rate was made 0–1000 cc min^{-1} at 20 °C, 0.1 MPa. The partial pressure of hydrogen and deuterium was obtained by using a quadrupole mass spectrometer. Gas and water concentration can be measured to 1 ppm and 500 ppb, respectively, in this system. The exit of the gas supply, the permeation test pipe, and the annular passage was equipped with a concentration measuring tube. The wall and gas temperatures were measured with a K-type thermocouple. The electric furnace was equipped with a R-type thermocouple for controlling heater temperature. In consideration of the errors induced by the thermocouples, scanner junction and DVM accuracy, the entire accuracy of the temperature measurement was within ±0.5 K.

The experimental procedure is as follows. At first, the gas mixture containing hydrogen is supplied to the annular passage without heating and a coefficient of transformation to change hydrogen partial pressure into hydrogen concentration is obtained by measuring hydrogen partial pressure. Next, helium gas is flowed into the permeation test pipe and the annular passage when hydrogen permeation is examined; on the other hand, argon gas is flowed into there when deuterium permeation is examined. Total gas pressure in the test section was set to be 0.1 MPa. The test section is heated and maintained a constant temperature. If the temperature of the permeation test pipe becomes constant for more than 30 min, this condition was assumed to the

Table 4
Experimental condition (hydrogen concentration and temperature)

Gas	Partial pressure [Pa]	Concentration [ppm]	Temperature [°C]					
			600	650	700	750	800	850
H_2/He	3.95×10^3	3.95×10^4	H-1	H-2	H-3	H-4	H-5	H-6
	1.01×10^3	1.01×10^4	H-7	H-8	H-9	H-10	H-11	H-12
	1.06×10^2	1.06×10^3	–	–	H-13,14	H-15,16	H-17–22	H-23
	1.17×10	1.17×10^2	–	–	–	–	–	H-24
D_2/Ar	4.04×10^3	4.04×10^4	–	–	D-1	D-2	D-3	D-4
	9.89×10^2	9.89×10^3	–	–	D-5,6	D-7,8	D-9,10	D-11–13

steady state. Then, the gas mixture was supplied to the permeation test pipe. An experimental condition is shown in Table 4. The parameter of the experiment was made a wall temperature of the permeation test pipe, hydrogen and deuterium partial pressure. The flow rate of the supply and the purge gas was set at 100 and 500 cc(STP) min^{-1}, respectively. Here, (STP) means standard temperature (0 °C) and pressure (0.1 MPa) condition.

3. Experimental results and discussion

A preliminary experiment was performed to confirm molecular diffusion in the gas mixture would not become the rate-limiting step of the hydrogen transport process. The variation in flow rate have no influenced on the amount of permeated hydrogen. The variation in the amount of permeated hydrogen was within 5.3% with flow rate ranging from 100 to 500 cc(STP) min^{-1}.

The longitudinal average temperature of the permeation test pipe can be obtained as follows. The measured points of wall and gas temperatures in the test section are shown in Fig. 5. Fig. 6 provides the wall and gas temperature distribution along the flow direction at the steady state condition. As shown in Fig. 5, the permeation test pipe, the measurement pipe, and the annular passage were equipped with 5, 9, and 5 thermocouples, respectively. As indicated in Fig. 6, it was found that wall temperature of the permeation test pipe (▲) and the measurement pipe (●), and the gas temperature (✳) of the annular passage in the same vertical position are almost equal. Thus, an average temperature of the permeation test pipe was obtained by using temperature at 11 measured points (A–K) assuming that the wall temperature of the permeation test pipe equals to that of the measurement pipe. The wall temperature in the center of the permeation test pipe is maintained at about 850 °C. Hydrogen permeability of Hastelloy X [11] in 600 °C decreases about 1/8 of the permeability in 850 °C and the surface area, which is less than 600 °C, is about 20% of the whole area. Thus, the amount of permeated hydrogen through the pipe, which is less than 600 °C, is about 1% of the one through the pipe, which is more than 600 °C. Therefore, the amount of permeated hydrogen from the low temperature part, which is lower than 250 K from the maximum temperature, was ignored. The

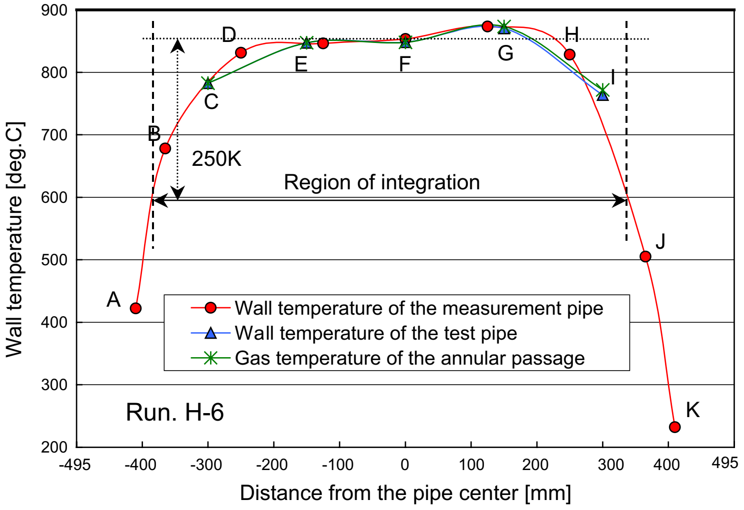

Fig. 6. Wall temperature distribution of the test and measurement pipes (H-6).

average temperature of the permeation test pipe was calculated by the trapezoid formula.

The permeation flux J [$m^3(STP)\,m^{-2}\,s^{-1}$] of hydrogen was obtained as follows. The relationship between hydrogen partial pressure in a gas phase and molar concentration of dissolved hydrogen on a surface of a pipe are assumed to obey Sieverts' law:

$$C_s = S\sqrt{p_{H_2}}, \tag{1}$$

where C_s is molar concentration of dissolved hydrogen. S [$m^3(STP)\,m^{-3}\,Pa^{-0.5}$] and p_{H_2} [Pa] is solubility and hydrogen partial pressure, respectively.

The permeation flux can be written as the following equation:

$$J = -D_s(r/r_i)(dC_s/dC_s), \tag{2}$$

where r [m] is radius of a circular pipe and D_s [$m^2\,s^{-1}$] is a diffusivity of hydrogen in a solid metal.

Substitution of Eq. (1) into Eq. (2) and integration of Eq. (2) gives:

$$J = \frac{K_p}{r_i \cdot \ln(r_o/r_i)}(\sqrt{p_i} - \sqrt{p_o}). \tag{3}$$

Here p_i and p_o [Pa] are hydrogen partial pressure in the permeation test pipe and the annular passage respectively; r_i and r_o [m] are an inner and an outer radius of the permeation test pipe. Hydrogen partial pressure in the permeation test pipe was assumed constant in this experiment. It is assumed that hydrogen partial pressure at the inlet of the annular passage is zero. Hydrogen partial pressure at the outlet of the annular passage is obtained by the mass spectrometer. Then, hydrogen partial pressure, p_o, in the annular passage is assumed an arithmetic mean value of hydrogen partial pressure at the inlet and outlet of the annular passage. K_p [$m^3(STP)\,m^{-1}\,s^{-1}\,Pa^{-0.5}$] is a permeability shown with the following equation:

$$K_p = D_s \cdot S = F_0 \exp(-E_0/RT), \tag{4}$$

where F_0 [$m^3(STP)\,m^{-1}\,s^{-1}\,Pa^{-0.5}$] and E_0 [$kJ\,mol^{-1}$] is a pre-exponential factor and an activation energy of hydrogen permeability. R [$J\,mol^{-1}\,K^{-1}$] is gas constant and T [K] is an absolute temperature of the pipe. An amount of permeated hydrogen Q [$m^3(STP)\,s^{-1}$] based on the inner radius of the permeation test pipe is shown by the following equation:

$$Q = 2\pi r_i l J = \frac{2\pi l K_{XR}}{\ln(r_o/r_i)}(\sqrt{p_i} - \sqrt{p_o}), \tag{5}$$

where l [m] is a pipe length and K_{XR} is the hydrogen permeability of Hastelloy XR.

The amount of permeated hydrogen, Q, was corrected by obtaining the amount of permeated hydrogen through the measurement pipe, Q_o:

$$Q_o = 2\pi r'_i L J_o = \frac{2\pi L K_X}{\ln(r'_o/r'_i)}(\sqrt{p_o} - \sqrt{p_a}), \tag{6}$$

where J_o is a permeation flux to the measurement pipe, K_X is the hydrogen permeability of Hastelloy X, p_o and p_a are hydrogen partial pressure in the annular passage and the outside of the measurement pipe. It is assumed $p_a = 0$ because of the outside of the measurement pipe being the atmosphere. L is the pipe length; r'_i and r'_o is the inner and outer radius of the measurement pipe. Wall temperature of the measurement pipe is assumed to be equal to the one of the permeation test pipe, and the reported value is used for the hydrogen permeability of Hastelloy X [11,12]. An effect on a decrease of the amount of permeated hydrogen by the oxide film will depend not only on a thickness but also on a state of formation of the oxide film. According to the reference [9,20], the effectiveness factor for reduction of permeability by the oxide film is reported to be 1/100–1/1000. The oxide film was already formed on the outside surface of the measurement pipe because it was being heated at about 700 °C under the atmospheric condition for more than 50 h before the experiment started. From the results of the amount of supplied and permeated hydrogen through the test pipe in the preliminary experiment, it was confirmed that the amount of permeated hydrogen through the measurement pipe becomes less than 1/10 of the value calculated with Eq. (6). If the amount of permeated hydrogen through the measurement pipe is overestimated, the hydrogen isotope permeability will be evaluated conservatively. One-tenth of the value calculated by Eq. (6) was corresponding to 3.6% of the amount of permeated hydrogen obtained by the experiment. However, since the thickness of the oxide film increases with increasing the heated time, the amount of permeated hydrogen will decrease. Therefore, the amount of correction value decreases with increasing the heated time any further. Though it is expected that the correction value is lower than 1/10 of the value calculated by Eq. (6), the reduction factor by the oxide film will be set to 1/10 from the view point of conservative aspect. The accuracy of the measurement and the correction value described above were included in the error of the pre-exponential factor.

The sum of the amount of permeated hydrogen, Q_e, obtained by the experiment and the correction value, Q_o, is assumed to be equal to the total amount, Q, obtained by Eq. (5). Then, K_{XR} becomes

$$K_{XR} = \frac{(Q_e + Q_o)\ln(r_o/r_i)}{2\pi l(\sqrt{p_i} - \sqrt{p_o})}. \tag{7}$$

Hydrogen permeability obtained in this experiment is shown in Fig. 7, and the activation energy and the pre-exponential factor are shown in Table 5. A solid line shows the average value of hydrogen permeability ob-

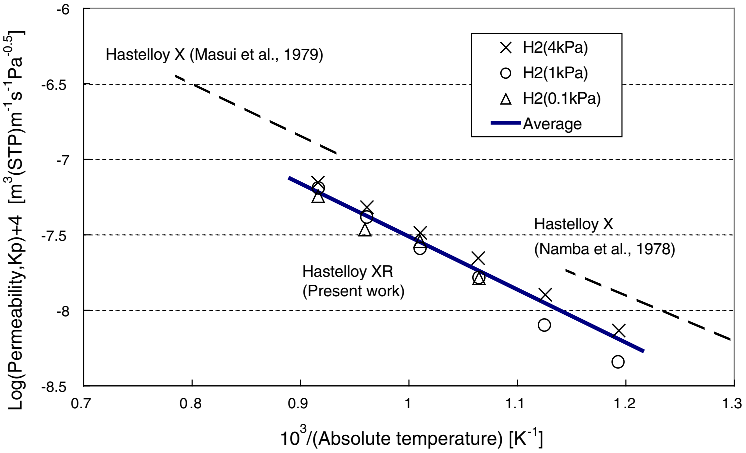

Fig. 7. Hydrogen permeability of Hastelloy XR and Hastelloy X.

Table 5
Activation energy and pre-exponential factor of permeability of H_2 and D_2

Gas species	Partial pressure [Pa]	Concentration [ppm]	Activation energy [kJ mol^{-1}]	Pre-exponential factor [m^3(STP) m^{-1} s^{-1} Pa$^{-0.5}$]
H_2	3.95×10^3	3.95×10^4	67.5	1.02×10^{-8}
H_2	1.01×10^3	1.01×10^4	68.1	1.01×10^{-8}
H_2	1.06×10^2	1.06×10^3	66.0	7.8×10^{-9}
H_2	Average		67.2 ± 1.2	$(1.0\pm0.2)\times10^{-8}$
H_2[a]	1.06×10^2	1.06×10^3	70.2 ± 2.0	$(4.7\pm0.4)\times10^{-9}$
D_2	4.04×10^3	4.04×10^4	76.1	2.31×10^{-8}
D_2	9.89×10^2	9.89×10^3	76.9	2.63×10^{-8}
D_2	Average		76.6 ± 0.5	$(2.5\pm0.3)\times10^{-8}$

[a] Some oxide film influence suspected.

tained by three kinds of hydrogen partial pressures. A dotted line shows hydrogen permeability of Hastelloy X [11,12]. The activation energy of hydrogen permeability of Hastelloy XR was almost equal to that of Hastelloy X. As the pre-exponential factor of hydrogen permeability of Hastelloy XR was smaller than that of Hastelloy X, hydrogen permeability of Hastelloy XR was also smaller than that of Hastelloy X.

Deuterium permeability of Hastelloy XR is shown in Fig. 8. How to calculate deuterium permeability is the same as the case of hydrogen permeability. According to the report [21], deuterium permeability becomes about $1/2^{0.5}$ times of hydrogen permeability. A dotted line in Fig. 8 shows hydrogen permeability at 3.95×10^3 Pa of hydrogen partial pressure. A solid line shows the approximate straight line obtained from deuterium permeability at 4.04×10^3 Pa (○) and 9.89×10^2 Pa (×) of deuterium partial pressure by a least square method. Deuterium permeability obtained by the experiment is shown in Table 5. The ratio of hydrogen permeability and deuterium permeability ($\beta(\mathrm{H/D}) = K_{\mathrm{PH}}/K_{\mathrm{PD}}$) is

$$\beta(\mathrm{H/D}) \approx (4.0 \pm 1.5) \times 10^{-1} \times \exp\{(9.4 \pm 1.7[\mathrm{kJ\,mol^{-1}}])/(\mathrm{RT})\} \qquad (8)$$

$\beta(\mathrm{H/D})$ becomes about 1.32 and 1.12 in 943 K (670 °C) and in 1093 K (820 °C), respectively. It was confirmed that the $\beta(\mathrm{H/D})$ decreases with increasing temperature for Hastelloy XR as same tendency as for stainless steel [18].

High purity helium gas (99.9999%) and argon gas (99.995%) were used as a purge gas to prevent an oxidation of the pipe surface. Both of the supply and the purge gas system were equipped with a molecular sieve trap (MST). In order to examine an effectiveness of oxide film for the permeability, the permeation test pipe was heated at 600–850 °C during 140 h under the condition of helium gas atmosphere and water concentration of less than 1 ppm. Fig. 8 shows hydrogen permeability of Hastelloy XR with the oxide film. The symbol of triangle (△) indicates these experimental data and the dotted-dashed line shows the average value of them. The activation energy and pre-exponential factor

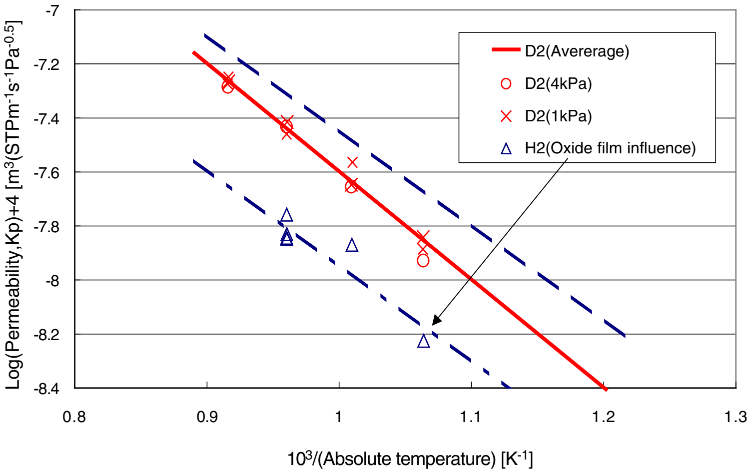

Fig. 8. Permeability of hydrogen and deuterium of Hastelloy XR.

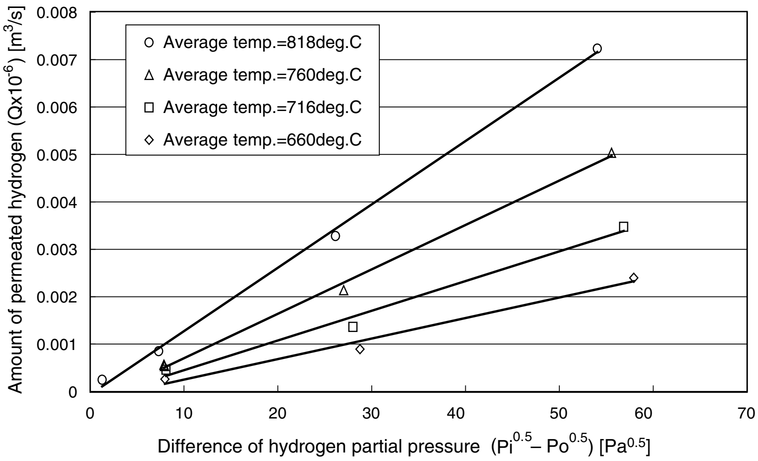

Fig. 9. Relationship between difference of partial pressure and amount of permeated hydrogen.

with the oxide film are indicated in Table 5. The effectiveness factor for reduction of permeability is about 0.3 in the present experiment. It is confirmed that a high temperature part of the pipe was discolored and oxidized. It is expected that the amount of permeated tritium also reduce by the oxide film in the HTTR hydrogen production system because the oxide film will be formed on the surface of the IHX heat transfer pipe during the initial period of the reactor operation.

The amount of permeated hydrogen is in proportion to the difference in square root of hydrogen partial pressure as far as the rate-limiting step of the transport process is diffusion in the solid metal even if hydrogen partial pressure decreases. That is, if the rate-limiting step of permeation becomes diffusion in the solid metal, the molar concentration of dissolved hydrogen on a surface of the pipe will obey Sieverts' law. Therefore, it is expected that a straight line connecting experimental data pass through a zero point. Fig. 9 shows a dependence on partial pressure to the amount of permeated hydrogen. A horizontal axis shows the difference in square root of the partial pressure. The straight line connecting experimental data for each average temperature passes through the neighborhood of zero point. Therefore, the amount of permeated hydrogen will be in proportion to the difference in square root of the partial pressure as for the low partial pressure area as well.

4. Conclusions

Experiment on hydrogen isotope permeation was performed to obtain permeability of hydrogen and deuterium of Hastelloy XR and to investigate the rate-limiting step of the process of hydrogen permeation phenomenon in the HTTR hydrogen production system. The following conclusions were obtained.

(1) The rate-limiting step of the hydrogen transport process in the HTTR hydrogen production system is diffusion in the pipe, except for the case that the oxide film is formed on the surface of the pipe. Therefore, the amount of permeated hydrogen isotope can be predicted by extrapolation in the low partial pressure region because a diffusion phenomenon in a solid metal is unchanged even if the number of hydrogen atom decreases.

(2) Hydrogen permeability of Hastelloy XR is as follows:

Average temperature of the pipe: 843–1093 K (570–820 °C)
Hydrogen partial pressure: 1.06×10^{2}–3.95×10^{3} Pa
Activation energy: $E_0 = 67.2 \pm 1.2$ [kJ mol^{-1}]
Pre-exponential factor: $F_0 = (1.0 \pm 0.2) \times 10^{-8} \times [\mathrm{m^3(STP)\,m^{-1}\,s^{-1}\,Pa^{-0.5}}]$.

(3) Deuterium permeability of Hastelloy XR is as follows:

Average temperature of the pipe: 943–1093 K (670–820 °C)
Deuterium partial pressure: 9.89×10^{2}–4.04×10^{3} Pa
Activation energy: $E_0 = 76.6 \pm 0.5$ [kJ mol^{-1}]
Pre-exponential factor: $F_0 = (2.5 \pm 0.3) \times 10^{-8} \times [\mathrm{m^3(STP)\,m^{-1}\,s^{-1}\,Pa^{-0.5}}]$.

(4) The ratio of an isotope effect between hydrogen and deuterium permeability is as follows, which showed a tendency to become small with increasing the temperature.

Average temperature of the pipe: 943–1093 K (670–820 °C)
Hydrogen P_H and deuterium P_D partial pressure: 1.0×10^{3}–4.0×10^{3} Pa
Ratio of the isotope effect:

$$\beta(\mathrm{H/D}) \approx (4.0 \pm 1.5)10^{-1} \times \exp\{(9.4 \pm 1.7[\mathrm{kJ\,mol^{-1}}])/(\mathrm{RT})\}.$$

(5) As hydrogen and deuterium permeability of Hastelloy XR were obtained for the first time, we can evaluate quantitatively the amount of permeated hydrogen isotope through the IHX prior to take the safety review for the construction of the HTTR hydrogen production system.

(6) Hydrogen permeability of Hastelloy XR after about 140-h heating under the less than 1 ppm water concentration was obtained. The effectiveness factor for reduction of permeability is about 0.3 in the present experiment. As it is expected that the oxidized film will be formed on the surface of the IHX heat transfer pipe, the amount of permeated hydrogen isotope through the pipes will be reduced in the HTTR hydrogen production system.

Acknowledgements

The gratitude is expressed to Professor M. Nishikawa of Interdisciplinary Graduate School of Engineering Science, Kyushu University for useful advice on the construction of hydrogen permeation test apparatus.

This research is the result of ‘development of technology for hydrogen production system’ of ‘development of nuclear heat utilization system technology’ carried out as study consigned from the Ministry of Education, Culture, Sports, Science and Technology.

References

[1] S. Saito, T. Tanaka, Y. Sudo, O. Baba, et al., Japan Atomic Energy Research Institute, JAERI Report JAERI-1332, 1994.
[2] S. Shiozawa, M. Ogawa, Y. Inagaki, S. Katanishi, T. Takeda, T. Nishihara, S. Shimizu, Y. Miyamoto, in: Proc. 12th Pacific Basin Nuclear Conf., Seoul, Korea, 29 October–2 November 2000, vol. 2, p. 1007.
[3] Y. Inagaki, T. Nishihara, T. Takeda, K. Hada, K. Hayashi, in: Proc. 7th Int. Conf. Nuclear Engineering, Tokyo, Japan, 19–23 April 1999, ICONE-7101.
[4] T. Takeda, J. Iwatsuki, Y. Inagaki, M. Ogawa, in: Proc. 7th Int. Conf. Nuclear Engineering, Tokyo, Japan, 19–23 April 1999, ICONE-7102.
[5] K. Sawa, H. Mikami, S. Saito, Energy 16 (1999) 459.
[6] R.A. Strehlow, H.C. Savage, Nucl. Technol. 22 (1974) 127.
[7] A.S. Zarchy, R.C. Axtmann, Nucl. Technol. 39 (1978) 258.
[8] A.S. Zarchy, R.C. Axtmann, J. Nucl. Mater. 79 (1979) 110.
[9] H.D. Rohrig, R. Hecker, J. Blumensaat, J. Schaefer, Nucl. Eng. Des. 34 (1975) 157.
[10] Y. Mori, T. Nakada, in: BNES Conf. on the HTR and Process Appl., Inst. of Civil Eng., Westminster, London, 26–28 November 1974, Paper 49.
[11] K. Masui, H. Yoshida, R. Watanabe, Trans. ISIJ 19 (1979) 547.
[12] T. Namba, S. Kokubo, M. Yamawaki, M. Kanno, J. Jpn. Inst. Metals 42 (1978) 374 (in Japanese).
[13] W.M. Robertson, in: Int. Meeting on Hydrogen in Metals, Julich, Germany, 20–24 March 1972, vol. II, p. 449.
[14] K. Hada, Y. Motoki, O. Baba, Japan Atomic Energy Research Institute, JAERI-M 90-148, 1990 (in Japanese).
[15] W. Steinwarz, D. Dtover, R. Hecker, W. Thiele, Nucl. Eng. Des. 78 (1984) 267.

[16] R.C. Reid, J.M. Prausnitz, B.E. Poling, The Properties of Gases and Liquids, 4th Ed., McGraw-Hill, New York, 1987, p. 582.
[17] Y. Fukai, H. Sugimoto, Adv. Phys. 34 (1985) 263.
[18] M. Nishikawa, T. Shiraishi, T. Yamaguchi, K. Kenmotsu, in: Proc. AESJ 1997 Spring Meeting, Tokyo, Japan, 24–26 March 1997, vol. 1, p. 120 (in Japanese).
[19] T. Takeda, J. Iwatsuki, T. Nishihara, in: Proc. 6th Int. Conf. Nuclear Engineering, San Diego, CA, USA, 10–14 May 1998, ICONE-6125.
[20] W.A. Swansiger, R. Bastasz, J. Nucl. Mater. 85&86 (1979) 335.
[21] H. Katsuta, K. Furukawa, J. Nucl. Sci. Technol. 18 (1981) 143.