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Permeation of multi-component hydrogen isotopes through austenitic stainless steels

Tomofumi Shiraishi *, Masabumi Nishikawa, Takahiro Yamaguchi, Kentaro Kenmotsu

Department of Nuclear Engineering, Faculty of Engineering, Kyushu University Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan

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Abstract

In a D–T fusion reactor tritium exists together with other hydrogen isotopes. However, the permeation of multi-component hydrogen isotopes through austenitic stainless steels has not been discussed so far. In this paper the permeation behavior of hydrogen isotopes through type 304 and 316 austenitic stainless steels was investigated by the co-current double tube method in the temperature range of 623–973 K. The permeabilities of hydrogen observed in this study gave close agreement with the recommended value by Le Claire. Discrepancies in reported values for the permeabilities of deuterium are larger than those of hydrogen and there has been no recommended value of permeability. The permeabilities of deuterium were obtained using the same apparatus and the same technique as hydrogen experiments. The isotope effect ratio in permeation for 316SS was smaller than that for 304SS. The permeation behavior of hydrogen isotopes in the binary-component hydrogen isotopes system was also observed under various conditions and compared with the values from the model calculation. It is concluded in this study that the separation factor in permeation through austenitic stainless steels coincides with the isotope effect ratio in permeation.

1. Introduction

One of the major problems in fusion technology is the permeation of tritium through metallic structural materials, especially austenitic stainless steels, because they are going to be used in various parts of a D–T fusion reactor.

Many works have been reported on the permeation of hydrogen through the membrane of austenitic stainless steels for the single-component hydrogen isotope system [1–23]. The permeabilities of H_2 were studied in most of these works and Le Claire has presented the recommended permeability which is derived by averaging the data of about forty investigators [23]. However, only a few researchers have reported the permeabilities of D_2 [2,5,8–11,19,22] and T_2 [12,16,17] through austenitic stainless steels. Accordingly, the reported values of isotope effect ratio in permeation of hydrogen isotopes through austenitic stainless steels are scarce and they cannot be said to be reliable.

Tritium handled in a D–T fusion reactor exists together with other hydrogen isotopes, protium and deuterium. However, there have been no discussions about the permeation behavior for the multi-component hydrogen isotopes through austenitic stainless steels.

The present authors chose type 304 and 316 austenitic stainless steels (304SS and 316SS) as the specimens in the present permeation study. The experimental results of the permeabilities of H_2 and D_2 in the single-component hydrogen isotope system were described at first. Then, the permeation behavior for the H_2–D_2 binary-component system in various conditions was discussed by comparing with the numerically estimated values. In this study a numerical calculation model using

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* Corresponding author. Present address: Hitachi Ltd., Power & Industrial Systems, R & D Division, 7-2-1 Omika-cho, Hitachi-shi, Ibaraki-ken 319-1221, Japan. Tel.: +81-294 23 5982; fax: +81-294 23 1963; e-mail: t-shira@erl.hitachi.co.jp.

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the finite difference method was applied to estimate the partial pressures of hydrogen isotopes in the axial direction of a permeation tube following the method stated in the previous works [24,25].

2. Experimental

The sizes and chemical compositions of 304SS and 316SS tube specimens used in this study are listed in Table 1. Before the permeation experiments, the specimens were gradually heated up to 973 K under the flow of helium gas with 20% H_2 for about 6 h. The co-current double tube method under the steady-state condition was also used in this experiment and the details of the experimental apparatus and techniques were described in the previous papers [24,25]. Temperature of the permeation membrane was changed from 623 to 973 K and the partial pressure of H_2 or/and D_2 in the process gas at inlet was changed from 19.8 to 1.01×10^5 Pa in the present study. Permeation check using the standard gas was performed at the beginning and the end of each experimental run. We made sure of the reproducibility of permeability from this observation which is that the permeability did not change during this experiment.

3. Results and discussion

3.1. Permeability of hydrogen isotopes through 304SS and 316SS

Fig. 1 shows the permeabilities of H_2 and D_2 through 304SS and 316SS at various temperatures. By the least-square method, the permeabilities are given by the following equations:

For 304SS,

$$K_H = 3.78 \times 10^{-7} \exp(-6.72 \times 10^4/RT), \qquad (1)$$

$$K_D = 4.34 \times 10^{-7} \exp(-7.18 \times 10^4/RT). \qquad (2)$$

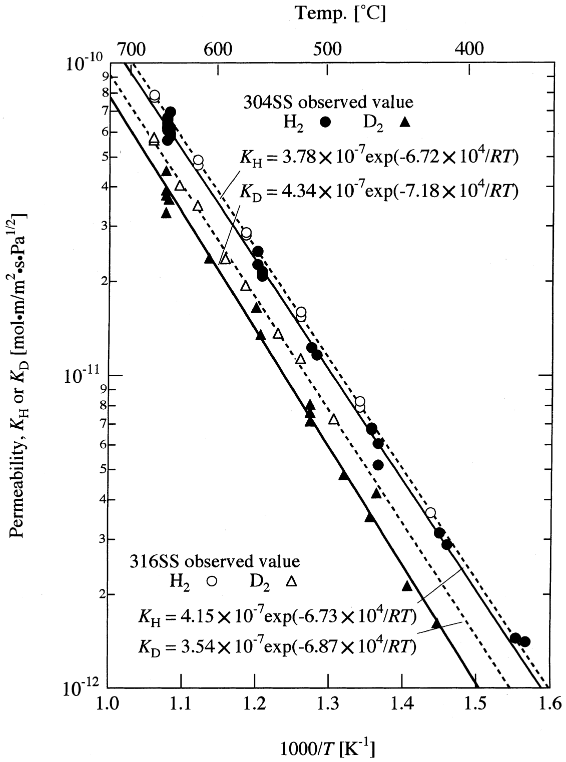

Fig. 1. Temperature dependence of H_2 and D_2 permeabilities through 304SS and 316SS.

For 316SS,

$$K_H = 4.15 \times 10^{-7} \exp(-6.73 \times 10^4/RT), \qquad (3)$$

$$K_D = 3.54 \times 10^{-7} \exp(-6.87 \times 10^{-4}/RT), \qquad (4)$$

where K_X (mol m/m^2 s Pa$^{1/2}$) is the permeability of hydrogen isotope X_2, R(J/mol K) is the gas constant, and T(K) is the absolute temperature. The calculated standard deviations were between 3.2% and 6.8%.

Permeabilities obtained in this study are compared in Figs. 2–5 with reported values [1–18,23]. It can be seen from these figures that the apparent activation energies

Table 1
Characteristics of specimens used in the present study

Specimen	Sizes length outer diameter thickness (mm)	Chemical compositions (wt%)								
		Fe	Cr	Ni	Mo	Mn	Si	C	P	S
304SS [a]	262.0 10.0 0.5	Balance	18	8	–	2	1	<0.08	<0.05	<0.03
316SS [b]	195.0 8.5 0.5	Balance	16.4	13.7	2.5	1.5	0.7	<0.05	<0.03	<0.01

[a] This Specimen was purchased from and analyzed by Nilaco.

[b] This specimen was developed and analyzed by Power Reactor and Nuclear Fuel Development Corporation (PNC).

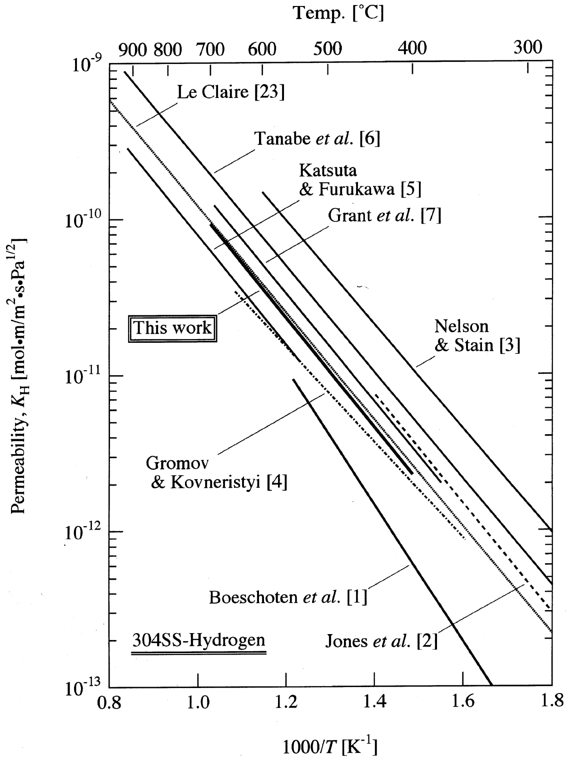

Fig. 2. Temperature dependence of H_2 permeability through 304SS. Permeability obtained in this study is compared with reported values.

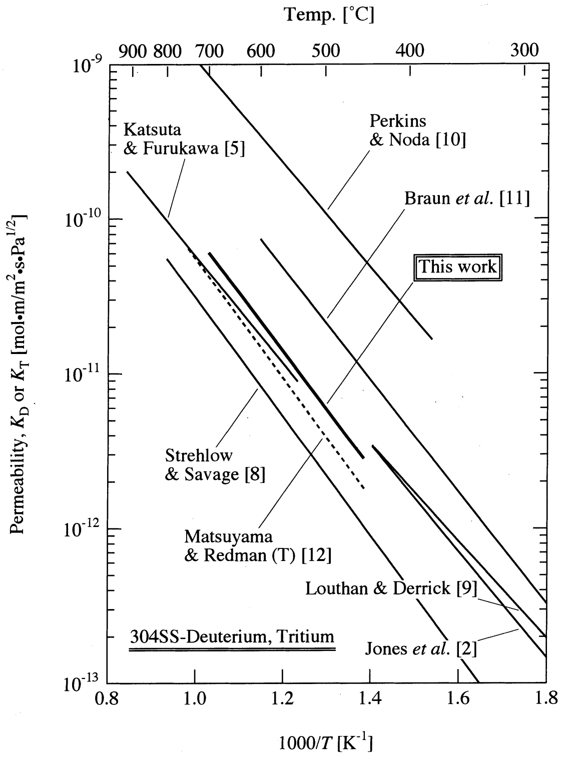

Fig. 3. Temperature dependence of D_2 and T_2 permeabilities through 304SS. Permeability obtained in this study is compared with reported values.

for the permeation of hydrogen isotopes through 304SS and 316SS obtained in this study are almost equal to the reported values.

Some authors have reported that hydrogen permeabilities through austenitic stainless steels are not so sensitive to the alloy composition [9,10,19,23]. Le Claire has reported that most data of H_2 permeabilities through austenitic stainless steels lie in a band within factors 1.5 and 1/1.5 of the mean value [23]. It can be seen from Fig. 1 that the permeability of H_2 through 316SS obtained in this study is about 10% larger than that through 304SS and they are close to the recommended value for austenitic stainless steels reported by Le Claire [23] as compared in Figs. 2 and 4. However, observations in this work show that the permeability of D_2 through 316SS is about 30% larger than that through 304SS within the experimental temperature range. Discrepancies in reported values for the permeabilities of D_2 through 316SS and 304SS are larger than those of H_2 as compared in Figs. 3 and 5, though there are only a few reports. The permeabilities of D_2 obtained in this study are considered to be reliable because they are obtained using the same apparatus and the same techniques as H_2 experiments. The permeability of D_2 through 304SS in this study lies between the value by Jones et al. [2] and that by Katsuta and Furukawa [5] and permeabilities by those authors are almost the same. We conclude that the permeabilities of D_2 in this study are also proper from the comparison in Fig. 3.

From the observations in the single-component experiment in this study, the isotope effect ratios in permeation of H_2 and D_2, $\beta_{\mathrm{P,H/D}}$ (dimensionless), are obtained as follows:

For 304SS,

$$\beta_{\mathrm{P,H/D}} = K_{\mathrm{H}}/K_{\mathrm{D}} = 0.870\exp(4.6\times10^{-3}/RT). \qquad (5)$$

For 316SS,

$$\beta_{\mathrm{P,H/D}} = K_{\mathrm{H}}/K_{\mathrm{D}} = 1.17\exp(1.4\times10^{3}/RT) \qquad (6)$$

and shown in Fig. 6 with the reported values for various types of austenitic stainless steels [2,5,14] [20–22]. The isotope effect ratio for 304SS of this study is similar to the values for 347SS reported by Gibson et al. [20]. Jones et al. [2] and Katsuta and Furukawa [5] have also reported the isotope effect ratio for 304SS, though their values show rather large difference. Furthermore, the temperature dependence of the isotope effect ratio in their study is different from the tendency of this study. The isotope effect ratio for 304SS of this study is a little

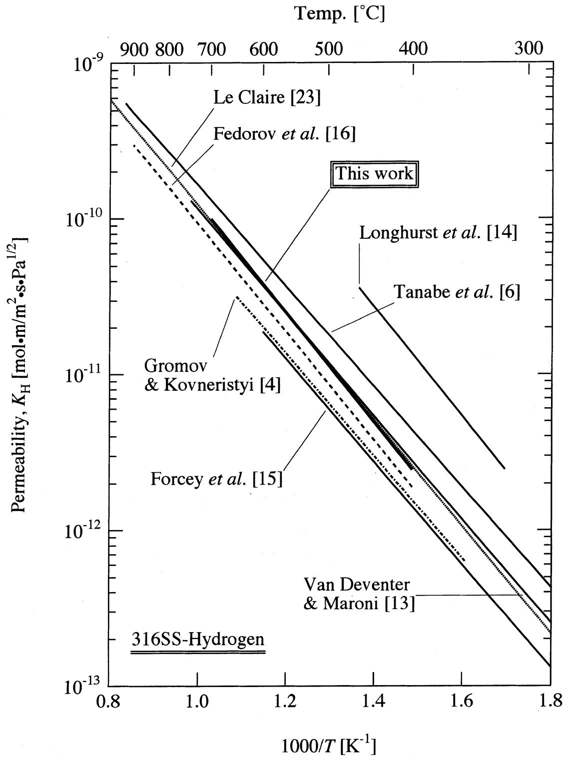

Fig. 4. Temperature dependence of the H_2 permeability through 316SS. Permeability obtained in this study is compared with reported values.

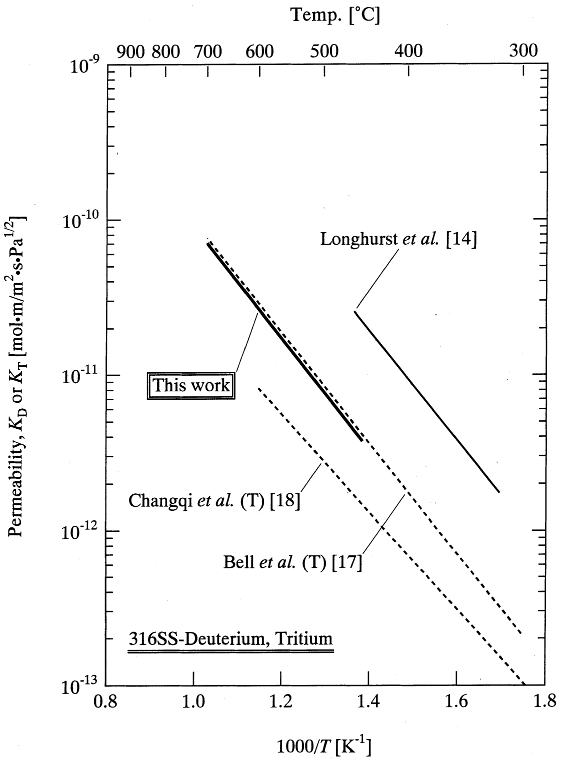

Fig. 5. Temperature dependence of D_2 and T_2 permeabilities through 316SS. Permeability obtained in this study is compared with reported values.

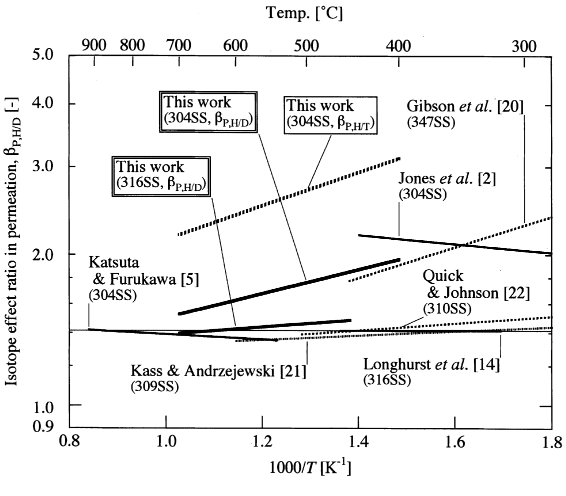

Fig. 6. Temperature dependence of the isotope effect ratios in permeation through 304SS and 316SS. Isotope effect ratios obtained in this study are compared with reported values for various types of austenitic stainless steels.

larger than the square root of the mass ratio that is said to be the ideal value of the isotope effect ratio. On the other hand, the isotope effect ratio for 316SS of this study is smaller than that for 304SS of this study and it is almost equal to $\sqrt{2}$ which is the value of the isotope effect ratio reported by Longhurst et al. [14]. The temperature dependence of the isotope effect ratio for 316SS is also smaller than that for 304SS. Further discussions with more data in relation to the alloy composition and permeation behavior of hydrogen isotopes are required, because there is a strong possibility that 316SS is used in various parts of a D–T fusion reactor.

We estimate the isotope effect ratio in permeation of H_2 and T_2, $\beta_{P,H/T}$, for 304SS from a comparison of the permeability of H_2 obtained in this study with the permeability of T_2 reported by Matsuyama and Redman [12] as follows:

$$\beta_{P,H/T} = K_H/K_T = 0.984\exp(6.5\times10^3/RT). \tag{7}$$

The isotope effect ratio varies from 2.19 at 973 K to 3.13 at 673 K and is larger than $\sqrt{3}$ as shown in Fig. 6. The permeability of T_2 through 316SS is reported by Bell et al. [17] and Changqi et al. [18]. In the estimation of the isotope effect ratio, $\beta_{P,H/T}$, for 316SS, however, their permeabilities cannot be used in this study because the permeability reported by Bell et al. seems to be a little bit large and that by Changqi et al. seems to be small. From the value of the isotope effect ratio, $\beta_{P,H/D}$, for 316SS in this study we have assumed that the isotope effect ratio, $\beta_{P,H/T}$, for 316SS is $\sqrt{3}$ which is the square root of the mass ratio.

Above observations on the isotope effect imply that use of 304SS piping is a better choice from the view point of suppression of tritium permeation.

We have already discussed the effect of the temperature distribution in a permeation membrane on the permeation behavior [25]. As can be seen from a comparison in Fig. 7, the material which has a large activation energy of permeation such as austenitic stainless steel is strongly influenced by the temperature distribution. In other words, improper use of the average temperature can give errors in quantification of permeabilities when the activation energy of permeation is large.

3.2. Permeation of multi-component hydrogen isotopes

The present authors have discussed the permeation rates in the binary-component hydrogen isotopes system in the case when diffusion controls the permeation by comparing three patterns in solubility (cases I–III) [24,25]. In discussion of these studies, that each hydrogen isotope acts independently in solution was assumed in case I, ideal solution with the isotope separation factor different from the isotope effect ratio in case II, and ideal solution with the isotope separation factor equal to the isotope effect ratio in case III.

An example of the experimental permeation rates of hydrogen isotopes through 316SS observed when both H_2 and D_2 are introduced to the permeation test section is shown in Fig. 8 with estimated values, where estimation is performed assuming case I or III for the solubility of hydrogen isotopes in 316SS in the binary-component hydrogen isotopes system. This figure shows the temperature dependence of the overall permeation rates observed under the conditions where the inlet partial pressure of H_2 to the inner channel was kept at 48.5 Pa and the inlet partial pressures of H_2 and D_2 to the outer channel were kept at 1.71×10^4 and 1.70×10^4 Pa, respectively. It is seen from this figure that the overall permeation rate of H_2 or D_2 becomes smaller than the value observed at the single-component system (case I) by about 30%. It can also be seen from this figure that the observed overall permeation rates agree well with the estimated values which are obtained by assuming case III.

Fig. 9 shows a comparison of estimated permeation rates applying case III with observed values in the binary-component system under various experimental conditions. Good agreement shown in this figure indicates that the application of case III to the permeation of binary-component hydrogen isotopes system through 304SS and 316SS is proper. Accordingly, it can be said that the separation factor in solubility is same as the isotope effect ratio and that diffusivities obtained at the single-component diffusion measurement is applicable to the binary-component diffusion in the partial pressure range of hydrogen isotopes of this study. The reason for

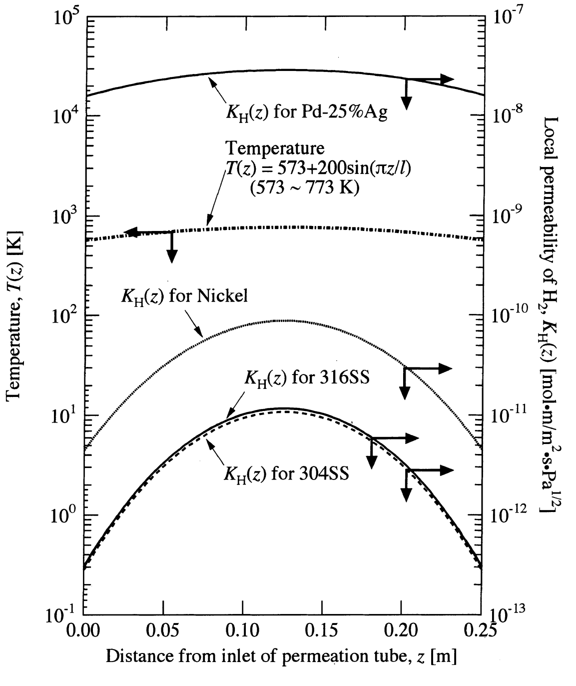

Fig. 7. Distributions of temperature and local permeabilities of H_2 for four materials as a function of distance from inlet of the permeation tube.

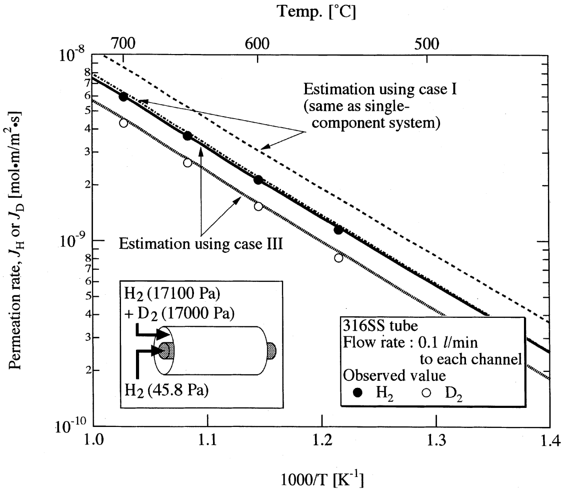

Fig. 8. Dependence of the permeation rates of H_2 and D_2 on the temperature of permeation membrane. The inlet partial pressure of H_2 to the inner channel was kept at 48.5 Pa and the inlet partial pressures of H_2 and D_2 to the outer channel were kept at 1.71×10^4 and 1.70×10^4 Pa, respectively.

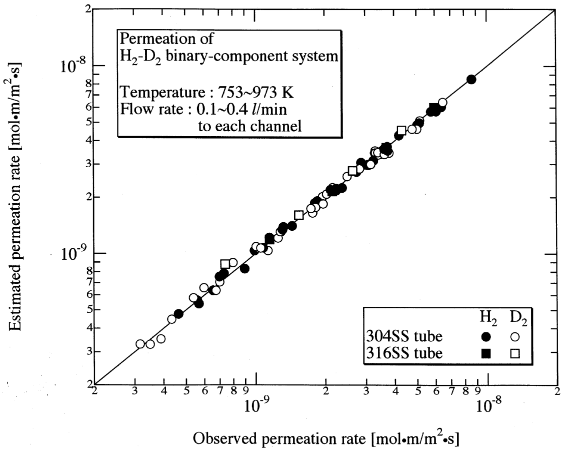

Fig. 9. Comparison of estimated permeation rates with observed values for H_2–D_2 binary component system.

these is that the interaction between hydrogen and deuterium is small because of the little solubility of hydrogen isotopes in austenitic stainless steels; the atomic ratio H/304SS is 2.8×10^{-4} at 773 K and 1.0×10^5 Pa of H_2 [6]. On the other hand, we have reported that the separation factor is different from the isotope effect ratio in such materials as palladium which has large solubility of hydrogen isotopes; the atomic ratio H/Pd is 6.8×10^{-3} at 773 K and 1.0×10^5 Pa of H_2 [26]. The authors consider that further discussions with more data on the solubility of the multi-component hydrogen isotopes system are necessary.

4. Conclusions

The permeabilities of H_2 and D_2 through 304SS and 316SS were determined by analysis of steady-state permeation using the co-current double tube method. The permeabilities of H_2 through 304SS and 316SS are in good agreement with the recommended value by Le Claire. The isotope effect ratios in permeation through 316SS are observed to be close to the square root of the mass ratios, though the isotope effect ratios in permeation through 304SS are much larger than the square root of the mass ratios.

The permeation behavior of hydrogen isotopes through 304SS and 316SS in the binary-component hydrogen isotopes system are observed and compared with the values from the model calculation. It is concluded in this study that the separation factor in permeation of the binary-component hydrogen isotopes through 304SS and 316SS is equal to the isotope effect ratio in permeation obtained from the single-component hydrogen isotope system.

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