Effect of Water Vapor on Permeation of Hydrogen Isotopes Through Pd-Ag Alloy

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1. INTRODUCTION

In order to operate the blanket as a system, it is important to understand the tritium behavior at the piping arrangement including a tritium recovery system as well as the behavior at the breeding part. Tritium behavior at the piping part can be influenced by water vapor because it has been certified that water vapor is released to the purge gas from solid breeders when hydrogen is added to the purge gas.

In this study, permeation behavior of hydrogen through Pd-Ag alloy in the water vapor atmosphere was measured. The effect of water vapor was represented by the local mass transfer coefficient at the boundary between gas phase and permeation membrane. In addition, tritium permeation behavior through Pd-Ag alloy or stainless steels was numerically estimated for the case of H₂⁻T₂ binary component system.

2. THEORY

The permeation behavior of hydrogen isotopes through the metal membrane consists of following steps;
1. Transfer of molecule from gas phase to the membrane through the boundary layer
2. Dissociation of molecule to atoms on the surface at the primary side
3. Transfer of atoms from the surface at the primary side to the bulk of the membrane (dissolution of gas in the metal)
4. Diffusion of atoms in the membrane along with the concentration gradient
5. Transfer of atoms from the bulk to the surface at the secondary side
6. Recombination of atoms to form molecule on the surface at the secondary side
7. Desorption of molecule from membrane surface

If water vapor exists in the gas phase, it can influence permeation behavior of hydrogen isotopes on the membrane surface. Therefore, gas phase mass transfer coefficients using properties in the gas phase at the primary/secondary side, representing 1, 2, 6 and 7, can express
its influence.

3. EXPERIMENTAL

A tube of palladium-25% silver alloy (80mm long, 4.8mm inner diameter and 5.0mm outer diameter, purchased from Nilaco Co.) was concentrically placed in a quartz tube (22mm inner diameter). 2% H₂/Ar was introduced to both inner and outer flow channel in order to activate the permeation membrane. After checking oxidation film was removed enough, sample gases were introduced to the inner and outer channel. Before introduced to the membrane, the sample gases were passed through water bubbler in order to be humidified. The bubbler was set in the incubator to keep constant temperature. The change of hydrogen pressure in the outlet gas was traced with time by gas chromatograph. The measurement was carried out until permeation attained steady state. Temperature of the permeation membrane was changed from 373 to 573K using electric furnace.

4. RESULT AND DISCUSSION

4-1) Experimental result

Diffusivity \( D_H [m^2/s] \) and solubility \( S_H [mol/m^3 Pa^{1/2}] \) of hydrogen in Pd-Ag alloy were obtained by permeation of dry hydrogen gas. The obtained values are expressed by following equations.

\[
D_H = 2.22 \times 10^{-7} \exp \left(-23.0 \frac{[kJ/mol]}{RT} \right) \quad (1)
\]

\[
S_H = 0.602 \exp \left(10.4 \frac{[kJ/mol]}{RT} \right) \quad (2)
\]

Fig. 1 shows the molar flux ratio of dry hydrogen to humidified hydrogen at the primary side. When water vapor exists in the gas phase, molar flux of hydrogen sharply dropped at lower temperature. The similar pattern was also observed at the secondary side. Considering this tendency, we got experimental equations of mass transfer coefficients both at the primary side (from gas phase to the membrane: \( k_1 [m/s] \)) and at the secondary side (from the membrane to the gas phase: \( k_2 [m/s] \)) as follows. \( k_{10} \) and \( k_{20} \) are mass transfer coefficients for dry hydrogen gas.

\[
\ln \left( \frac{k_1}{k_{10}} \right) = -8.66 \times 10^{-6} P_{water} \exp \left(16.3 \frac{[kJ/mol]}{RT} \right) \quad (3)
\]

\[
\ln \left( \frac{k_2}{k_{20}} \right) = -1.61 \times 10^{-5} P_{water} \exp \left(15.9 \frac{[kJ/mol]}{RT} \right) \quad (4)
\]

4-2) Estimation of tritium permeation in H₂-T₂ binary component system

In H₂-T₂ binary component system, concentration of hydrogen and tritium in the membrane are expressed by following equations. Therefore, solution should be considered properly. That is, solution and diffusion should be dealt with separately by dividing the membrane into the small pieces like Fig. 2 shows.

\[
q_H = S_H Y_H P_{total}^{1/2} \quad (5)
\]
$$q_T = S_T y_T P_{total}^{1/2} \quad (6)$$
Where \( y_H = P_H/(P_H + P_T) \), \( y_T = P_T/(P_H + P_T) \), \( P_{total} = P_H + P_T \)

4-2-1) **For the case of Pd-Ag alloy (under dry condition)**

Figs. 3-4 show that how permeation of tritium is affected by hydrogen when 1Pa tritium with 100Pa hydrogen is constantly introduced to the membrane. As to tritium, outlet partial pressure and concentration in the membrane have a peak before attaining steady state. This phenomenon is characteristic of binary component system caused by solubility difference of hydrogen and tritium.

Fig. 5 shows that how 1Pa tritium is influenced by addition of hydrogen. Under such condition, permeation of tritium attains equilibrium at steady state after breakthrough regardless of hydrogen concentration. The amount of dissolved tritium decreases as hydrogen concentration gets higher as shown by eq.(6). The reduction of tritium dissolution makes tritium breakthrough earlier though it reduces tritium permeation rate. That is, it makes tritium permeation through the membrane to the secondary side earlier than the case for existing only tritium in this case.

The case for \( H_2-T_2 \) binary component system together with water vapor is estimated in Fig. 6. According to this estimation, water vapor doesn’t influence tritium permeation behavior very much at steady state above 473K although it influences the peak height. Therefore, Pd-Ag membrane can be used for tritium recovery at normal temperature (around 573K) even though water vapor exists in the gas phase.

4-2-2) **For the case of stainless steel (under dry condition)**

Estimation of tritium permeation behavior through stainless steel such as 316SS and F82H-mod. can be also discussed in a similar way. Diffusivity and solubility of hydrogen isotopes in 316SS and F82H-mod. have been reported previously [1-5]. We suppose that piping system consists of plural tubes and the gas is constantly introduced to the piping system.

Fig. 7 shows outlet partial pressure of tritium at the secondary side to compare tritium permeation through 316SS with through F82H-mod. Tritium permeates more through F82H-mod. than through 316SS. Therefore, 316SS is more proper for piping material than F82H-mod. in terms of less tritium permeation.

Figs. 8-9 show that how hydrogen influences tritium permeation in F82H-mod. Fig. 8 is for the case that tritium permeation doesn’t get equilibrium at steady state after breakthrough. In this case, reduction of tritium dissolution makes tritium permeation rate slow, which results into reducing tritium permeation. On the other hand, Fig. 9 is for the case that tritium permeation gets equilibrium at steady state after breakthrough even if hydrogen exists. In this case, hydrogen accelerates tritium permeation since reduction of tritium dissolution makes tritium breakthrough point earlier though it reduces tritium permeation rate. This case is
similar to Fig. 5. Taking these estimations into account, addition of hydrogen can reduce or accelerate tritium permeation, which depends on the condition. Therefore, it is important to design the piping system as tritium permeation doesn't get equilibrium at steady state after breakthrough. Otherwise, hydrogen will help tritium permeation.

5. References
Fig. 5 Effect of hydrogen on tritium permeation

Fig. 6 Effect of water vapor on tritium permeation

Fig. 7 Outlet partial pressure of tritium at the secondary side

Fig. 8 Effect of hydrogen on tritium permeation through F82H-mod. (1000K, linear velocity=0.368m/s)

Fig. 9 Effect of hydrogen on tritium permeation through F82H-mod. (1000K, linear velocity=0.05m/s)