Study on Hydrogen Transport into Ni, W, Cu and STS Metal Membranes using Current Transient Technique†

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Hydrogen transport behaviours through the metals such as nickel, tungsten, copper and stainless steel have been investigated using the electrochemical hydrogen permeation method. The results show that hydrogen permeation current through the nickel increased as the charging potential increased. Hydrogen diffusion coefficient of metals was calculated from the hydrogen permeation transient profile. From the experimental results, it was realized that the flux of hydrogen permeating the metal depends on the metal composition and on the applied charging potential.

Key Words: Hydrogen transport, Charging potential, Permeation transient, Diffusion coefficient.

INTRODUCTION

It has been well known that hydrogen can be easily absorbed into the metal matrix *via* many processes such as fabrication, welding and corrosion and cathodic polarization[1]. Hydrogen transport into the metal matrix has been generally investigated using the electrochemical permeation method[2-4].

Electrochemical hydrogen permeation technique was first developed by Devanathan and Stachurski[5]. Since then, this electrochemical technique has been widely used by many researchers to determine hydrogen permeation behaviour due to its ease and simplicity[6-8]. In this study, we investigated the electrochemical hydrogen permeation behaviour to prepare the hydrogen-implanted samples of nickel, tungsten, copper and stainless steel. They are considered as the materials of the first wall of international thermonuclear experimental reactor (ITER).

EXPERIMENTAL

Nickel, tungsten and copper with thickness of 50 μm and stainless steel with thickness of 15 μm were used as metal membranes, respectively. All of the metals were purchased from Nilaco (Japan) in + 99.9 % and mechanically polished with silicon carbide paper of 1800 grit to eliminate the surface oxide films and then washed with ethanol and distilled water.

For the permeation of hydrogen into the metals, the Devannathan and Stachurski cell composed of two compartments was used as shown in Fig. 1. The metal as a metallic membrane was clamped between the compartments. In the first compartment, a constant cathodic potential was applied to generate adsorbed hydrogen on the surface of the metal by water reduction. In the second compartment, the anodic potential was applied to maintain a zero hydrogen concentration on this surface. A 0.1 N NaOH solution of pH 13 was used as the electrolyte and de-aerated by bubbling with argon gas in both compartments. The exposed surface area of the metal membrane was 1.766 cm^2 in both sides. For composing the electrochemical measurement system, a platinum wire (99.9 %) was used as the counter electrode and an Ag/AgCl electrode was served as the reference electrode; both were placed directly in the cell and connected to a potentiostat (Bio-Logic SAS). All experiments were carried out at ambient temperature.

RESULTS AND DISCUSSION

Mechanism of hydrogen permeation reaction: The electrochemical hydrogen permeation is accompanied by hydrogen evolution reaction (HER) which affects the current efficiency. There are generally two accepted mechanisms for hydrogen evolution reaction reaction. One is Volmer-Tafel mechanism by step (1) and (2).

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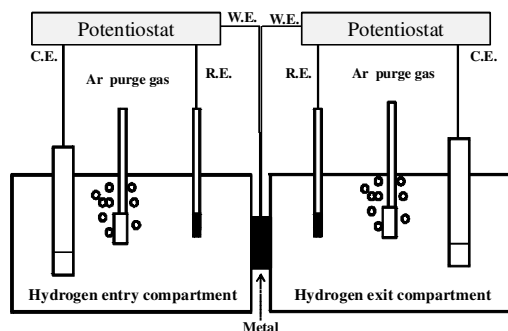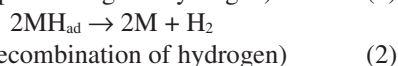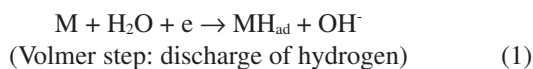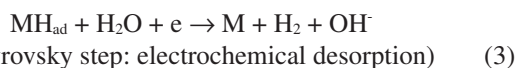
Fig. 1. Schematic of the electrochemical hydrogen permeation cell

$$M + H_2O + e \rightarrow MH_{ad} + OH^-$$
(Volmer step: discharge of hydrogen)   (1)
$$2MH_{ad} \rightarrow 2M + H_2$$
(Tafel step: recombination of hydrogen)   (2)

The other is and Volmer-Heyrovsky mechanism by steps (1) and (3).

$$MH_{ad} + H_2O + e \rightarrow M + H_2 + OH^-$$
(Heyrovsky step: electrochemical desorption)   (3)

Most of the adsorbed hydrogen reacts to form molecular hydrogen and releases to the atmosphere through reaction (2) or (3) and at the same time, some fraction of adsorbed hydrogen is permeated into the metal matrix[9,10].

$$MH_{ad} \rightarrow M(H_{ab})$$
     (4)

Hydrogen permeation current density: The cyclic voltammogram was performed on the nickel electrode to determine the optimal potentials for the hydrogen charging and the oxidation of hydrogen. Fig. 2 shows a cyclic voltammogram measured at nickel electrode in a 0.1 N NaOH solution at a scan rate of 20 mV s^{-1}. In Fig. 2, for the scan towards positive potential, an oxidation wave emerged at 0.3 V$_{Ag/AgCl}$, in the reverse scan the cathodic current wave corresponding to the reduction occurred at 0.13 V$_{Ag/AgCl}$. In addition, typical reduction of water into molecular hydrogen was observed at potentials lower than -1.10 V$_{Ag/AgCl}$.
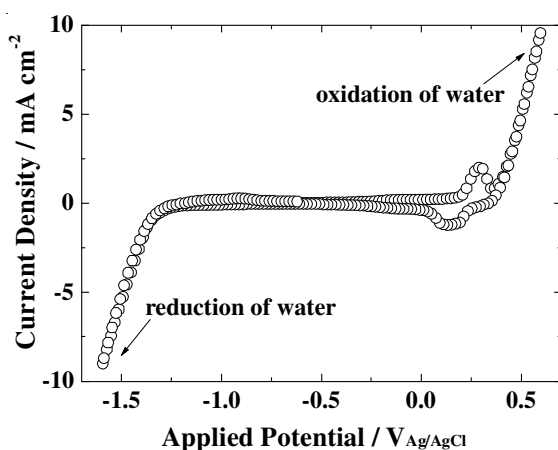
Fig. 2. Cyclic voltammogram obtained from the nickel electrode in a 0.1 NaOH solution with a scan rate 20 mV s^{-1}

To perform the electrochemical permeation experiment, the charging potential to generate adsorbed hydrogen on nickel surface has to be adjusted below -1.10 V$_{Ag/AgCl}$, while the anodic potential has to be applied to be oxidized to H$^+$ in the range between -0.5 and -0.1 V$_{Ag/AgCl}$.

To investigate the effect of the charging potential on the hydrogen permeation, a series of cathodic potentials were applied to the side of the cathodic compartment and the potential of the anodic compartment was kept at a constant to be -0.2 V$_{Ag/AgCl}$. Fig. 3 shows the current transients of hydrogen permeation with the nickel specimen obtained from the current transient technique in a 0.1 N NaOH solution.
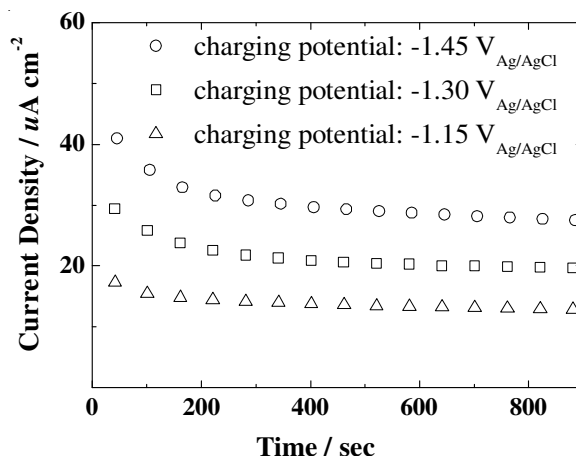

Fig. 3. Current density of hydrogen permeation through the nickel membrane as a function of the charging time

In Fig. 3, the steady-state permeation current density increased with an increase of the cathodic potential. This indicates that an increase of the charging potential leads to an increase of the density of the adsorbed hydrogen on the nickel surface by reduction of water. And the increase of the density of the adsorbed hydrogen leads to an increase of the hydrogen diffusion into the nickel matrix.

In order to compare with the hydrogen permeability of test metals, the electrochemical current transient technique was performed on nickel, tungsten, copper and stainless steel. Fig. 4 shows the permeation current transients as a function of permeation time for nickel, tungsten, copper and stainless steel, respectively. In Fig. 4, the steady-state current densities of the metal specimens exhibit 27, 200, 27 and 29 μA cm^{-2} for nickel, tungsten copper and the stainless steel, respectively. In particular, the current density value of the tungsten was higher than those of other metals.
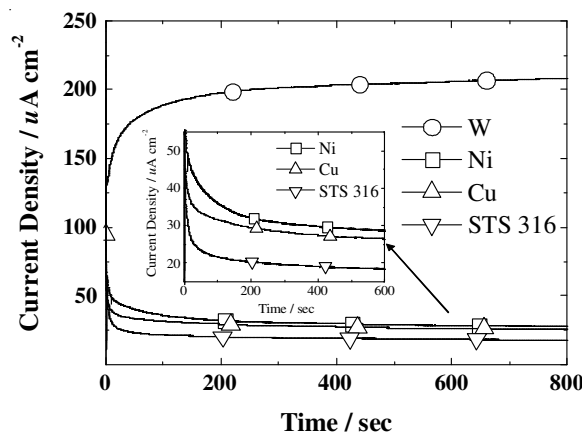
Fig. 4. Current transients of hydrogen permeation for W, Ni, Cu and STS 316 at a hydrogen charging potential of -1.45 V$_{Ag/AgCl}$ (Ni), -1.5 V$_{Ag/AgCl}$ (W), -1.4 V$_{Ag/AgCl}$ (Cu) and -1.2 V$_{Ag/AgCl}$ (STS 316)

Evaluation of the permeation parameter: To calculate the diffusion coefficient D (cm^2 s^{-1}) from the permeation current transient obtained from the oxidation of hydrogen atom in anodic compartment, we used the equation (5) proposed by Gileadi *et al.*[11] and McBreen *et al.*[12]:

$$D = 0.138 \ L^2/t_{0.5} \qquad (5)$$

where, $t_{0.5}$ is half of the time to a steady state value and L is the thickness of the metal membrane.

Hydrogen diffusion coefficients for nickel, tungsten, copper and stainless steel are 1.16×10^{-8}, 1.86×10^{-8}, 1.15×10^{-8} and 9.8×10^{-9} cm^2 s^{-1}, respectively. In general, it was known that hydrogen permeation behaviour depends on both the hydrogen diffusion coefficient and the adsorbed hydrogen concentration on the metal surface. The hydrogen diffusion coefficient determines the ability for hydrogen to permeate through a metal, while the adsorbed hydrogen concentration determines how hydrogen absorbs into a metal matrix. Therefore, from the comparison of the hydrogen permeation current transient and the diffusion coefficient, it was thought that the tungsten metal has good hydrogen permeability.

Conclusion

It was observed that the hydrogen permeation current through the nickel membrane increased as the applied potential increased cathodically. This indicates that the hydrogen charging potential raises the density of the adsorbed hydrogen on nickel surface. And then the increase of the adsorbed hydrogen density is a driving force of the hydrogen diffusion into the nickel matrix. In addition, the diffusion coefficients of nickel, tungsten, copper and stainless steel were calculated using hydrogen permeation transients obtained from the oxidation of hydrogen atom in anodic compartment. From the comparison of the hydrogen permeation current transients and the diffusion coefficients of metals, it is expected that the tungsten has a good performance for the hydrogen permeation.

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