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Hydrogen permeability measurement through Pd, Ni and Fe membranes

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Abstract

An ultrahigh vacuum apparatus for the measurement of hydrogen gas permeation through metal membranes has been developed to perform studies in the ranges of low pressure and medium temperature. The sealing of the hydrogen gas at the specimen is done by gold O-rings which yield vacuum tightness. The hydrogen permeation is measured for pure Pd, Ni and Fe membranes over a pressure range of 0.1–100 mbar and a temperature range of 50–440°C. The results are compared with data in the literature. It shows that the permeation is exceedingly affected by the surface contamination on the specimens in the case of Pd. The contaminants are taken off from the Pd surface by short aging around 200–300°C in air. After cleaning the surface, the permeation amount increases and agrees well with the literature data. The activation enthalpies for permeation are (0.144±0.003), (0.600±0.003) and (0.382±0.004) eV for Pd, Ni and Fe, respectively, in the present investigation. For Ni and Fe, such a special treatment to clean the surface is not necessary.

Keywords: Hydrogen absorbing materials; Gas–solid reactions; Diffusion

1. Introduction

Permeability measurements in many solids have been carried out using the gas permeation method which is a powerful method, especially for hydrogen gas [1–3]. However, not always good agreement between the permeation results has been found. This fact is caused, at least partly, by surface limited mass transport. Recently, considerable refinements have been made in the techniques for classical permeation measurements. The most important one is the use of an ultrahigh vacuum apparatus — with which the surface contamination has decreased during and before measurements. Even with an ultrahigh vacuum apparatus, in many cases the specimen was welded to a holder [4] (for example to a Cu gasket [5]). However, surface modification and/or surface damage is possible. Such a treatment must be avoided to obtain precise permeability results. In many past studies, the permeation measurements were limited to high hydrogen pressure and temperature and to thick specimens in order to decrease the effect of surface contamination. In the present work, the use of an ultrahigh vacuum apparatus allowed us to measure at low pressure and temperature and to use thin foils.

In the present study, an apparatus was developed for gas permeation used in ultrahigh vacuum with a mass spectrometer. The apparatus was used for measurements of hydrogen permeation through palladium, nickel and iron specimens at low pressures and medium temperatures. The specimen was mounted to the apparatus without being welded to the holder.

2. Experimental procedure

A schematic diagram of the apparatus for the permeation measurements is shown in Fig. 1a. Both sides of the specimen, i.e. up-stream (inlet side) and down-stream (outlet side) for hydrogen gas were evacuated to ultrahigh vacuum by turbo-molecular pumps and then hydrogen gas was introduced in the inlet side and automatically controlled to the desired pressure by a pressure controller. The partial pressure of hydrogen on the outlet side was measured by a quadrupole mass spectrometer together with the partial pressures of other gases. For helium a secondary electron multiplier was used for ion detection. The enlarged figure, Fig. 1b, shows the part around the specimen together with flanges which support the specimen. The

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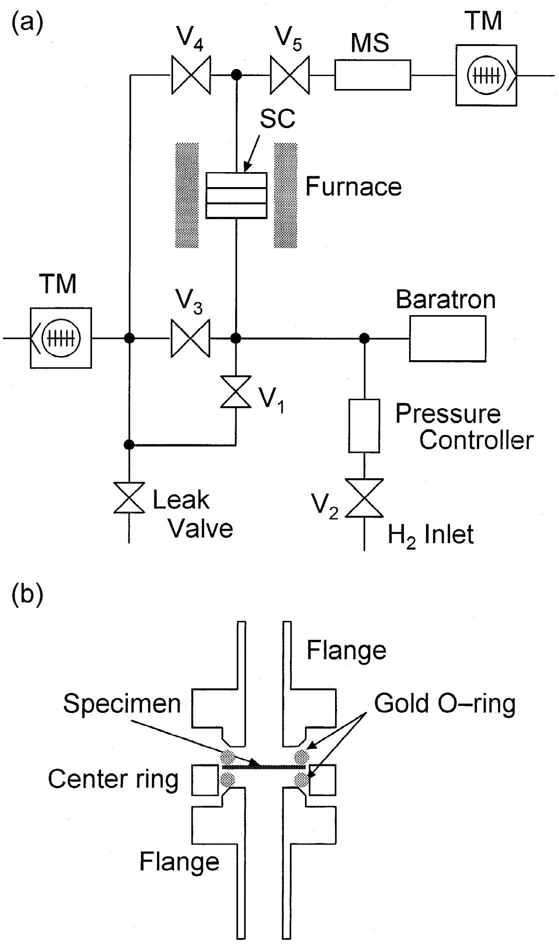

Fig. 1. Schematic diagram of experimental apparatus. (a) Block diagram: TM = turbo-molecular pump, SC = specimen chamber, MS = analyzer tube of mass spectrometer, V_1 = variable leak valve, V_2~V_5 = valve. (b) Part of the specimen and supporting flanges.

sealing for the gas was well done with gold O-rings on both sides of the specimen. With this arrangement, it was possible to measure permeation below hydrogen pressures of 100 mbar at the inlet side and below temperatures of 440°C. The pressure on the outlet side could be measured in the range of 10^{-10}–10^{-4} mbar. The lowest and highest pressures on the inlet side are dependent on the base pressure on the outlet side at evacuated condition and on the saturation limit of the detection of the mass spectrometer, respectively. The temperature of the specimen was automatically controlled by a temperature controller and a small furnace, which surrounded the supporting flange of the specimen wrapped by Cu blocks. The temperature of the specimen was measured using K-type (Alumel-Chromel) thermocouples.

The hydrogen gas on the inlet side was always evacuated through a bypass line with a variable leak valve to constantly renew the hydrogen gas in order to suppress the accumulation of non-penetrating gases.

The foil materials of pure metals used in the present experiment were purchased from W.C. Heraeus Ltd. (Hanau, Germany) for Pd and Goodfellow Metals Ltd. (Huntingdon, England) for Ni and Fe. The thickness of the foils was 100 μm (Pd), 125 μm (Ni) and 90 μm (Fe), respectively. Nominal purity of the materials was 99.9+% for Pd, 99.99% for Ni and 99.95% for Fe. Discs of 20 mm in diameter were punched out from foils of the pure materials. They were ultrasonically washed in acetone and rinsed in alcohol. After this treatment the Pd specimens were annealed in vacuum at 700°C for 3 h. For Pd, some of the specimens were not annealed (hereafter called as-received specimens). Other treatments were done for some of the Pd specimens as mentioned in Section 4. The Ni and Fe specimens were annealed at 850°C in flowing hydrogen gas for 14 h.

After mounting the specimen in the specimen chamber, two types of experiments were carried out. First, the saturation pressure (steady state pressure) of hydrogen on the down-stream side (outlet side) was measured for various constant pressures of hydrogen on the up-stream side (inlet side) for a constant temperature. Second, the saturation pressure on the outlet side was measured for various constant temperatures of the specimen at a constant pressure on the inlet side.

After mounting the specimen, the cleaning procedure of the Pd specimen surface was done in situ, by aging of the specimen in air. The specimen was heated up to a temperature between 80 and 350°C in vacuum and then air was introduced into the apparatus. After 3–5 min the apparatus was evacuated again. Then the hydrogen gas was introduced into the inlet side and the permeation measurements were started.

3. Analysis

On steady state condition of the pressure on the outlet side, the flux of diffusing hydrogen, J, is expressed by the following equation [5],

$$\begin{aligned} J &= (A/d) J_0 P_i^{1/2} \exp(-Q_J/kT) \\ &= (A/d) K_{sp} P_i^{1/2} \exp(-Q_s/kT) D_0 \exp(-Q_D/kT) \qquad (1) \end{aligned}$$

where A, d, J_0, Q_J, P_i, K_{sp}, Q_s, D_0 and Q_D are the surface area of the disc for permeation, thickness of the disc, pre-exponential coefficient for permeation, activation energy for permeation, pressure on inlet side, solubility constant, heat of solution for hydrogen, pre-exponential factor in diffusion and activation energy for hydrogen diffusion, respectively.

In the present investigation the saturation pressure on the outlet side was measured at various constant pressures on the inlet side and various specimen temperatures. The amount of the hydrogen permeation, J, is related to the saturation pressure as follows: The saturation pressure at the desired temperature of the specimen was measured on the outlet side at a constant pumping speed of the turbo-molecular pump. The saturation pressure, p, is expressed by

$$p = J/S + p_o \tag{2}$$

where S and p_o are the pumping speed and the ultimate pressure of the system, respectively. If the ultimate pressure, p_o, is considerably smaller than the saturation pressure, p, J can be treated as proportional to p. In the present case, p_o is in the range of 10^{-10} mbar. Therefore, in a considerably wide range of temperature and pressure, p_o can be neglected in the present experiment. By comparison of the present data with literature data for Pd, Ni and Fe [5–7], the pumping speed in the present case can be estimated as 100 l/s as will be mentioned later.

4. Results and discussion

In the present investigation, the pressure of hydrogen on the outlet side gradually increased to the value of steady state if the pressure of hydrogen on the inlet side was kept constant. An example of the time dependence of pressure on the outlet side for a Ni specimen is shown in Fig. 2 for consecutively higher temperatures of the specimen at a constant pressure on the inlet side. The pressure on the outlet side increases as the temperature increases to the next constant temperature and then gradually approaches the saturation pressure at this temperature.

The saturation pressure was measured as a dependence of the pressure on the inlet side at a constant temperature. The logarithm of the saturation pressure for a Pd specimen is shown in Fig. 3 against the logarithm of the pressure P_i on the inlet side for different temperatures. These specimens were submitted to different annealing treatments. In Fig. 3, as-received Pd specimen was annealed at 700°C in vacuum for 3 h and then mounted on the permeation apparatus. Full marks show the permeation results without surface cleaning treatment for this specimen. Open marks show the results after annealing in air in order to clean the surface. The surface cleaning treatment was done by aging in air at 300°C (Fig. 3a) and at various temperatures between 80 and 250°C (Fig. 3b). Each set of data is on a straight line except for a range of high pressure near 10^{-4} mbar and the full marks in Fig. 3b. The line made by full marks shows a steeper slope than the lines of open marks (Fig. 3a). The deviation from the line at high pressures and temperatures was caused by the saturation limit of the mass spectrometer.

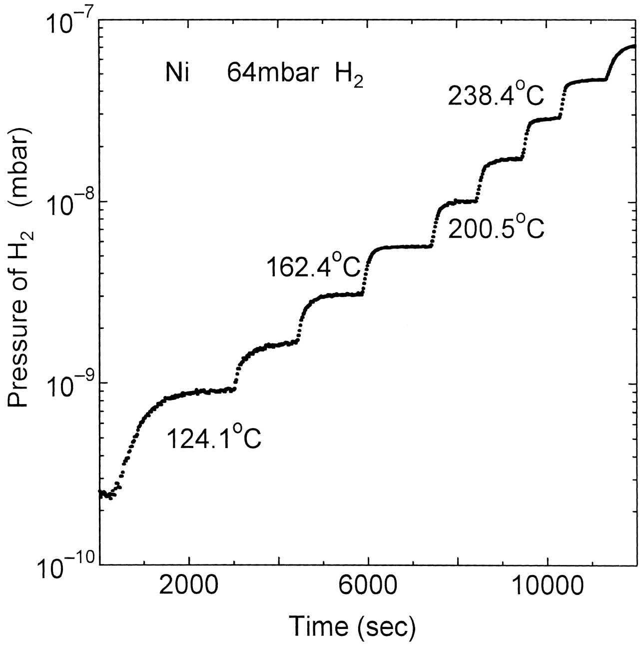

Fig. 2. An example of the pressure change at the down-stream side (outlet side of permeated hydrogen) for a Ni specimen against time for various temperatures. The ordinate is shown in logarithmic scale.

The permeation results in the literature through Pd foils show large scattering due to surface contamination of the specimen [8,9]. The effects of contamination on the surface for Pd were elaborately reviewed by Musket [10]. He discussed treatment for minimizing the effects, surface controlled permeation and diffusion controlled permeation. For the surface controlled permeation, the relation, $J \propto P_i$ holds and for diffusion controlled permeation $J \propto P_i^{1/2}$ where P_i is the pressure of hydrogen on the inlet side, as already mentioned, i.e. the slope of the line in log–log plot is larger than 1/2 depending on the degree of the surface contamination. Amano et al. [11] and Yoshida et al. [12] also discussed the surface contamination of the Pd membrane by adsorption of impurity gases. On the basis of the discussion by Musket, Amano et al. and Yoshida et al., in the present study the cleaning of the surface by annealing the specimen in air was attempted. Annealing temperatures between 80 and 350°C were applied. The slope of the relation, p vs. P_i, in Fig. 3b considerably decreases with increasing annealing temperature and finally becomes 0.55 at around 200°C for the annealing temperature. The amount of permeation increased after the cleaning procedure especially at low pressures on the inlet side as shown in Fig. 3b.

For the specimen with a clean surface, the law of Sieverts should hold ($J \propto P_i^{1/2}$). In fact, the slope of the saturation pressure in Fig. 3a is 1.1 for the specimen that did not undergo the cleaning treatment and 0.53–0.56 for the specimen after cleaning.

The logarithms of the saturation pressure for as-received Pd specimens are shown in Fig. 4 against reciprocal temperature at a constant pressure (1.0 mbar) on the inlet side. For all measurements shown in the figure, the saturation pressure was always measured from low-temperature to high-temperature. The marks (except circle) show the data for the specimen without any cleaning treatment after the specimen was mounted in the apparatus. The circle marks show the data for the specimen after surface cleaning. The marks (except circle) in Fig. 4 show

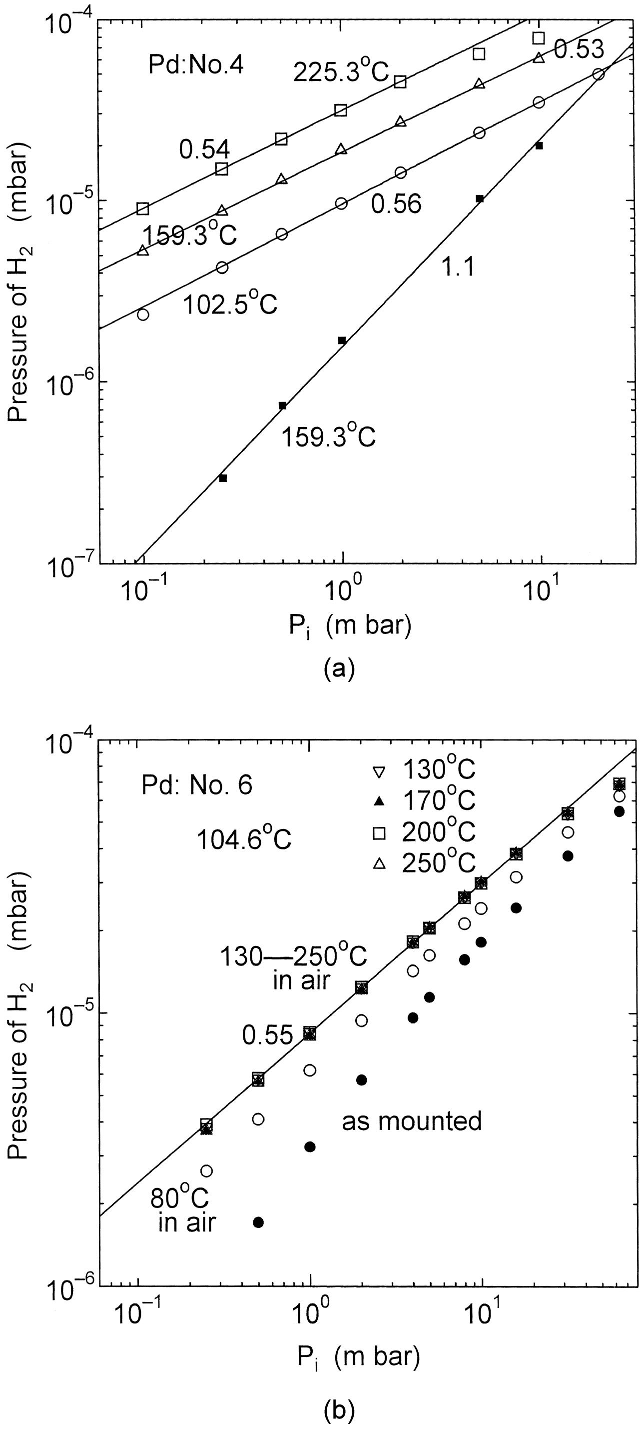

Fig. 3. Saturation pressure on the outlet side against pressure on the inlet side for the Pd specimens. The ordinate and abscissa are shown in logarithmic scales. The data points are on a line at each temperature except high temperature and pressure, and the line for the specimen with contaminated surfaces shows a steeper slope than for clean surfaces. Full marks show the results for untreated specimens after mounting on the apparatus and open marks show those after cleaning in air. (a) Data for untreated specimens after mounting on the apparatus and for aged specimens in air at 300°C. The numbers indicate the specimen temperature and the slope for the best fit. (b) Data for untreated specimens and for aged specimens in air at 80–250°C. The temperatures after the marks indicate the aging temperature in air. All the runs of permeation were measured at 104.6°C.

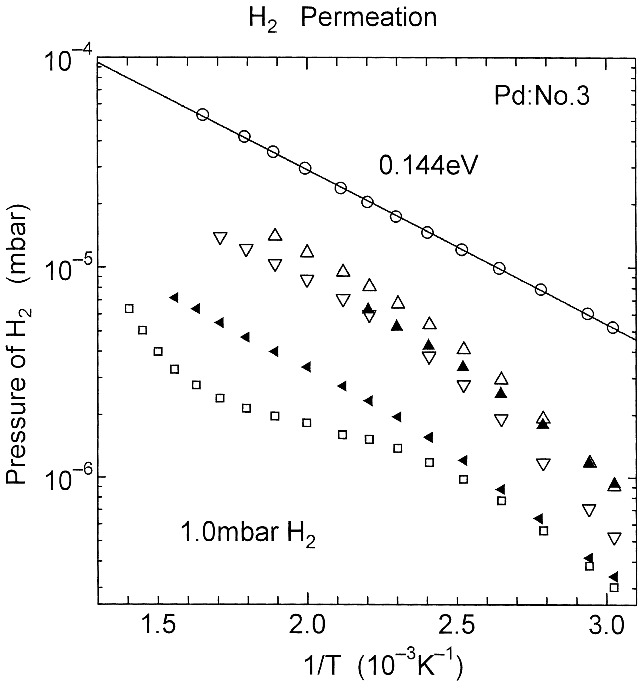

Fig. 4. Saturation pressure on the outlet side for a Pd specimen against the reciprocal of the temperature at a constant pressure on the inlet side (1.0 mbar). The marks (except circle) show the results for untreated specimens after mounting on the apparatus and circle marks show those after cleaning in air. The measurements were repeated several times up to successively higher maximum temperatures for the untreated specimen. The maximum temperatures, T_{max}, were ▲, 180.6°C; △, 255.4°C; ▽, 312.2°C; ◀, 368.7°C and □, 438.7°C, respectively. The slope of the straight line corresponds to 0.144 eV.

complex behavior. The measurements were repeated several times, up to successively higher maximum temperatures for the measuring run. The permeation amount gradually decreased even at the same temperature with increase of the maximum measuring temperature except the case between the first (▲) and second (△) run. For the last run without surface cleaning in the figure (□), the amount of permeation exceedingly decreased exhibiting a stage around 230°C ($1.7\times10^{-3}<1/T<2.4\times10^{-3}$ K^{-1}). On the other hand, the circle marks are on a straight line for a wide temperature range. Furthermore, the amount of the permeation is about one order of magnitude larger than in the last run mentioned before.

This complex behavior can be explained as follows: The contaminants adsorbed on the walls of the specimen chamber were desorbed with successive heating of the specimen and then they were adsorbed on the surface of the specimen. In fact, in many cases after the total pressure in the outlet side largely increased and decreased during the heating, the amount of permeation decreased considerably.

Hydrogen permeation results for Pd were reported by Koffler et al. [5]. Their activation enthalpy for permeation was (0.162±0.002) eV. Their ranges of temperature and pressure were from 27 to 436°C and from 3.9×10^{-4} to 6.7×10^{-2} mbar, respectively. In this range of hydrogen pressure [13–15], the α-phase in the Pd–H system is stable. They showed that hydrogen flux, J, followed the law of Sieverts and the logarithm of J showed a linear relation against the reverse temperature. The present results for the specimen annealed in air show good agreement with their results. In the present study, the saturation pressure p in the outlet side can be expressed for a Pd membrane by the equation

$$p\,[\mathrm{mbar}] = 3.20 \times 10^{-6}(A/d)\, P_{\mathrm{i}}^{1/2} \exp(-0.144\,[\mathrm{eV}]/kT) \tag{3}$$

The ranges of temperature and pressure were from 50 to 430°C and from 0.5 to 15 mbar, respectively. The temperature ranges depended on the pressure because of the saturation limit of the mass spectrometer. For example, in the case of 1.0 and 5.0 mbar for the pressure on the inlet side, the temperature ranges were from 50 to 430°C and from 50 to 280°C, respectively. In these ranges, the Pd–H system is also certainly in the α-phase. From comparison of the present results with the results of Koffler et al., the pumping speed of our apparatus was estimated as 100 l/s.

In the case of Ni at low temperatures, the pressure on the outlet side increased gradually and normally it took very long time to reach saturation. Therefore, the measurements of the Ni specimens to check the validity of the law of Sieverts and to collect the data for permeability were done at comparatively higher temperatures than those for the Pd specimens. For the Ni specimens the saturation pressures of hydrogen on the outlet side were measured as dependent on the hydrogen pressure on the inlet side at four different temperatures. In Fig. 5, the pressures on the outlet side are shown against the pressures on the inlet side with logarithmic scales. The slope of each line is nearly equal to 1/2 which means that the law of Sieverts is valid for this specimen.

The saturation pressure was obtained for various temperatures at constant pressure (4, 16 or 64 mbar) on the inlet side and is drawn against the reciprocal of the temperature as shown in Fig. 6, together with the data for 0 mbar (vacuum). Each set of data is on a straight line. The slope of the line shows good agreement with the results of Robertson [6]. His activation enthalpy for permeation was (0.568±0.001) eV. In his study, the ranges of temperature and pressure were from 24 to 500°C and from 1013 to 3040 mbar, respectively. For the present experiment, the residual pressure in the apparatus is not negligible for the data points at low temperatures. Therefore, the residual hydrogen pressure for the case of vacuum is subtracted from the data and the results are shown in Fig. 6. Then a better agreement with the lines is obtained also at low temperatures. The pressure, p, can be expressed for Ni by the equation

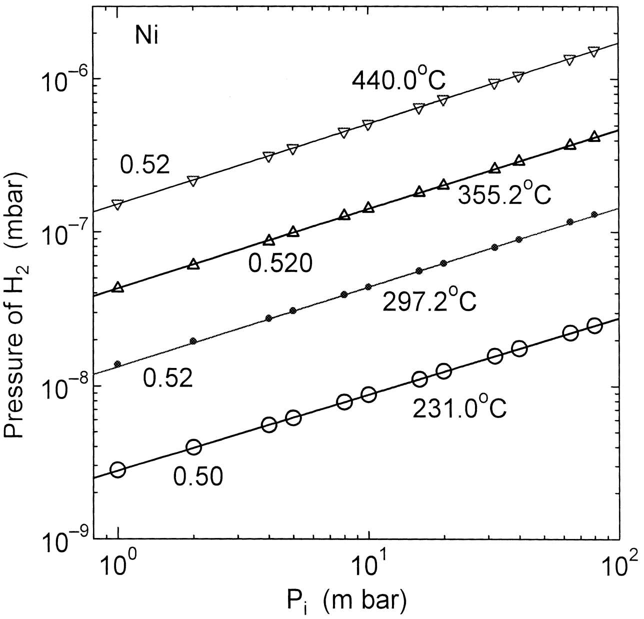

Fig. 5. Logarithm of saturation pressure on the outlet side for Ni specimens against the logarithm of the pressure on the inlet side at four constant temperatures.

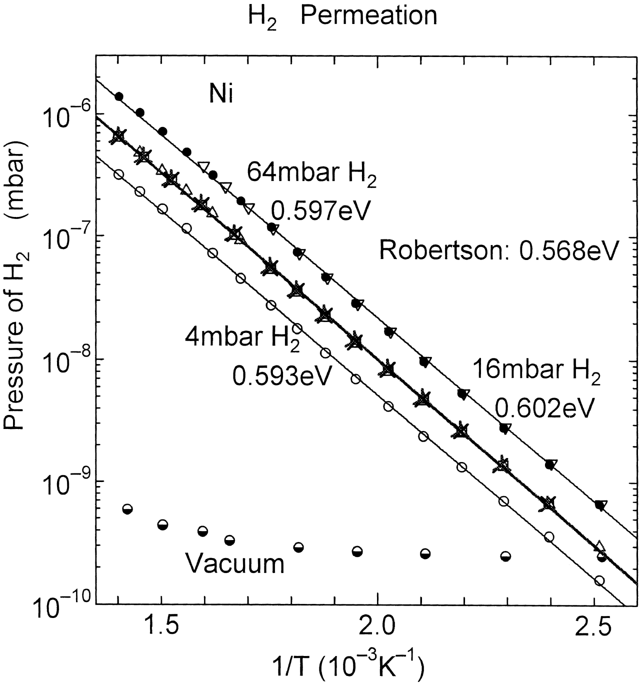

Fig. 6. The logarithm of saturation pressure on the outlet side for Ni specimen against the reciprocal temperature for three constant pressures on the inlet side together with the pressure for the vacuum condition. The marks on the middle line show the data for 16 mbar H_2. The data after subtracting the residual hydrogen pressure are shown. The activation enthalpies are shown for the present results and Robertson's results [6].

$$p\ [\text{mbar}] = 1.40 \times 10^{-5}(A/d)P_i^{1/2}\exp\left(-0.600\ [\text{eV}]/kT\right) \tag{4}$$

The ranges of temperature and pressure were from 4 to 64 mbar and from 125 to 440°C, respectively. From comparison with the data of Robertson, the pumping speed of our system was estimated as 100 l/s.

For the case of the Fe specimens, the saturation pressures on the outlet side are shown in Fig. 7 against various hydrogen pressures on the inlet side for three constant temperatures of the specimen. The slope of each line is nearly equal to 1/2, as in the case of Ni and cleaned Pd. In Fig. 8, the saturation pressure is shown against the reciprocal temperature for two constant pressures. Each set of data is on a straight line. The slope of the line shows good agreement with the data of Gonzalez [7], as shown later. His activation enthalpy for permeation was (0.367±0.004) eV. In his study, the ranges of temperature and pressure were from 49 to 506°C and from 43 to 628 mbar, respectively. In the present study, the pressure p for Fe can be expressed by

$$p\ [\text{mbar}] = 1.30 \times 10^{-6}(A/d)P_i^{1/2}\exp\left(-0.382\ [\text{eV}]/kT\right) \tag{5}$$

The ranges of temperature and pressure were from 85 to 375°C and from 4 to 64 mbar, respectively. From comparison with the data of Gonzalez, the pumping speed of our system can be estimated as 100 l/s.

The estimated pumping speed for our system is the same for Pd, Ni and Fe. This fact guarantees that our apparatus has enough efficiency for the permeation measurements.

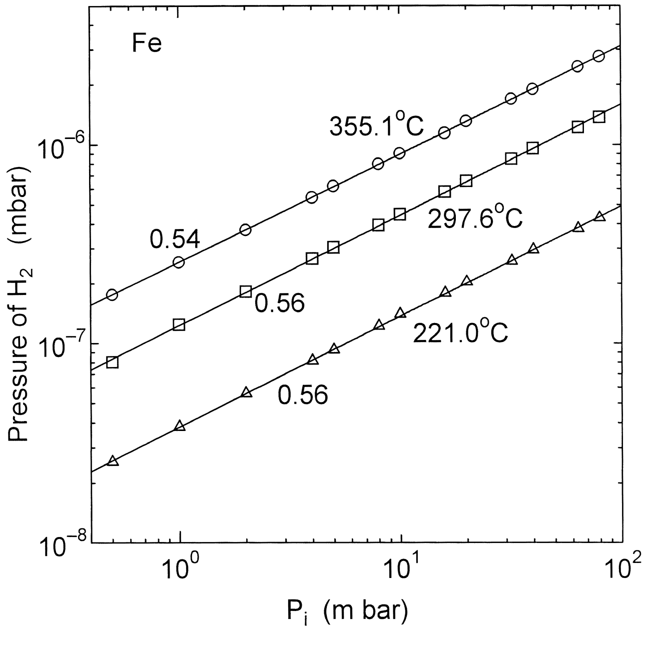

Fig. 7. The logarithm of saturation pressure on the outlet side for the Fe specimens against the logarithm of the pressure on the inlet side at three constant temperatures.

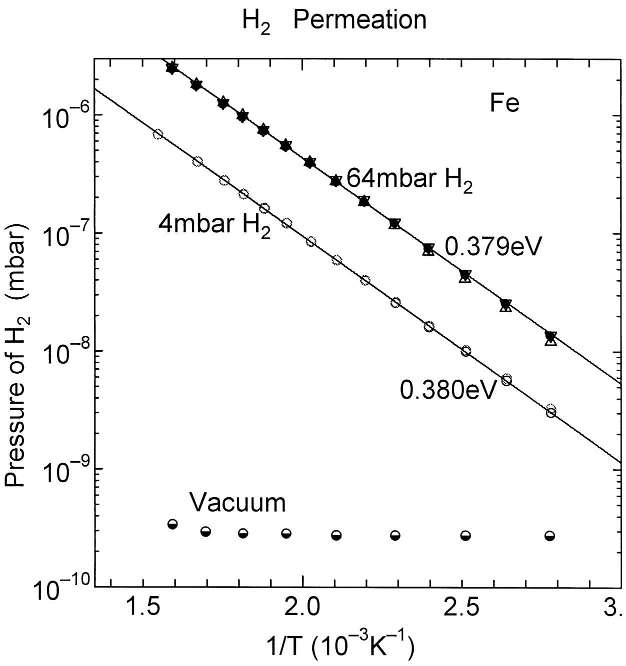

Fig. 8. The logarithm of saturation pressure on the outlet side for the Fe specimens against the reciprocal temperature for two constant pressures (4 and 64 mbar) together with the pressure for the vacuum condition on the inlet side.

The annealing of the specimens in the permeation apparatus at 80 and 200°C in air was carried out for the Ni specimens and at 80°C in air for the Fe specimens. The amount of hydrogen permeation decreased after annealing in air and then gradually recovered to the previous values during the long exposure to hydrogen gas. The annealing of Ni and Fe in air has no enhancing effect on the hydrogen permeation, which is different from the case of Pd.

Finally, the data of the present investigation are shown in Fig. 9, together with the results available in the literature. The marks show the present raw data and the lines show the results by Koffler et al. [5], Robertson [6] and Gonzalez [7]. The literature data are adjusted to the same pumping speed (100 l/s) for all three metals. The thickness of the specimens was 100 μm (Pd), 125 μm (Ni) and 90 μm (Fe), respectively. The data of $P_i = 4$ mbar are shown in the figure because many experiments in the present case were done at 4 mbar and for comparison, the data at other pressures were normalized to 4 mbar by the relation $p \propto P_i^{1/2}$. The number in the figure near the mark indicates the pressure, P_i, at which the experiment was performed. The deviation of data points from the line in the case of Ni at low temperatures is caused by the base pressure of hydrogen in the vacuum condition because the raw data shown in this figure are different from the case of Fig. 6, i.e. the data points show the values without subtraction of the base pressure. Considering the corrected

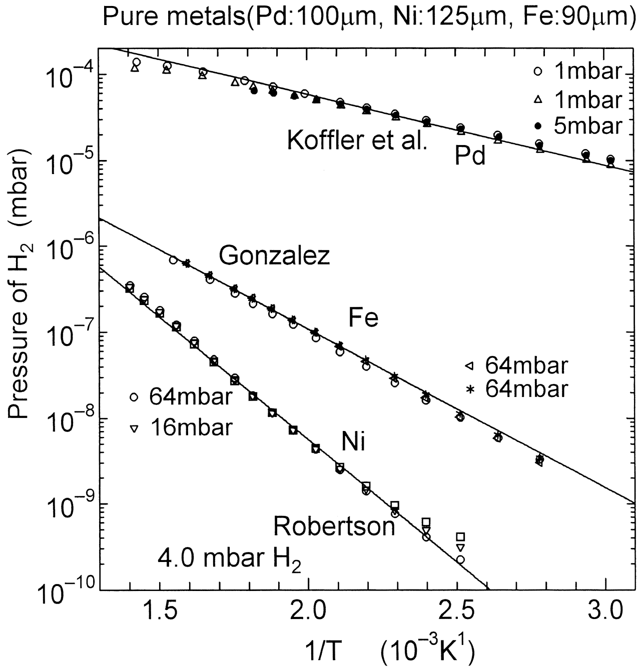

Fig. 9. The logarithm of saturation pressure on the outlet side for Pd, Ni and Fe specimens against the reciprocal of temperature at constant pressures. The thickness of the specimens are 100 μm (Pd), 125 μm (Ni) and 90 μm (Fe), respectively. The marks show the data of the present investigation for $P_i = 4$ mbar and data normalized to 4 mbar for other pressures as indicated. The lines are calculated from the literature data (Koffler et al. [5], Robertson [6] and Gonzalez [7]) assuming a pumping speed of 100 l/s.

values, better agreement is obtained also at low temperatures in the case of Ni, as mentioned before.

Summarizing, it can be stated that the present data for Pd, Ni and Fe show good agreement with the literature results.

In conclusion, the permeation of hydrogen gas is effectively measured by the presented permeation apparatus. The contaminated surface of Pd specimens became gradually clean after annealing in air. A check of the validity of the law of Sieverts is useful to disclose surface contamination. For a contaminated surface, the slope of the line is close to 1, whereas for a clean one it is 1/2. For Pd, surface contamination is removed by annealing in air at around 200–300°C.

The activation enthalpies of permeation are determined as (0.144±0.003), (0.600±0.003) and (0.382±0.004) eV for Pd, Ni and Fe, respectively, for specimens with cleaned surfaces. These values agree well with the literature data for Pd, Ni and Fe and therefore the presented permeation apparatus is powerful for the measurement of hydrogen permeation through membranes. In a following report, results for hydrogen gas permeation through multilayers of Pd–Fe and Pd–Ni systems will be published.

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