S_n = the nth distance of the Fourier image from the grating
t = time
t_a = time between successive arrivals of the dispersed phase at the laser
$\vec{U}$ = resultant velocity of the particle
U_y, U_z = velocity components in the y and z directions
U_{TB} = velocity of Taylor bubbles
U_D^s = superficial velocity of the dispersed phase
U_G^s = superficial velocity of the gas phase
Z = dimensionless distance from the center of the particle to the center of the laser beam
Z^* = dimensionless distance from the grating to the image plane

Greek Symbols

α = angle between light ray and the normal to particle interface
• = maximum possible error in detecting particle chord as diameter
η = dimensionless slit distance
λ = wavelength
ϕ = distribution function for the light field
τ = transit time of the particle passing through slot beam

LITERATURE CITED

Azzopardi, B. J., "Measurement of Drop Sizes," Int. J. Heat and Mass Tr. **22**, 1245 (1979).

Ballic, E. A., and Chan, J. H. C., "Fringe Image Technique for the Measurement of Flow Velocities," *Appl. Optics*, **12**, 2603 (1973).

Chan, J. H. C., and Ballic, E. A., "SNR in Optical Velocimeters: Effect of Particle Number Density," *Appl. Optics*, **14**, 1839 (1975).

Chan, J. H. C., and Ballic, E. A., "Application of Fourier Images to the Measurement of Particle Velocities," *Appl. Optics*, **13**, 234 (1974).

Durst, F., and Zaré, M., "Laser Doppler Measurements in Two Phase Flows," *Proc. of the LDA-Symposium*, Copenhagen, 4-3-429 (1975).

Farmer, W. M., "Observations of Large Particles with a Laster Interferometer," *Appl. Optics*, **13**, 610 (1974).

Farmer, W. M., "Measurement of Particle Size and Concentrations Using LDV Techniques," *Proc. of the Dynamic Flow Conference*, Marseille, France (1978).

Fristram, R. M., Jones, A. R., Schwar, M. J. R. and Weinberg, F. J., "Particle Sizing by Interference Fringes and Signal Coherence in Doppler Velocimetry," *Faraday Symposia Chem. Soc.*, **7**, 183 (1973).

Goodman, J. W., *Introduction to Fourier Optics*, McGraw-Hill (1968).

Hacker, D. S. and Hussein, F. D., "The Application of a Laser Schlieren Technique to the Study of Single Bubble Dynamics," *Ind. Eng. Chem. Fund.*, **17**(4), 277 (1978).

Lee, S. L., and Srinivasan, J., "Measurement of Local Size and Velocity Probability Density Distributions in Two Phase Suspension Flows by Laser Doppler Techniques," *Int. J. Multiphase Flow*, **4**, 141 (1978).

Papoulis, A., "Probability, Random Variables and Stochastic Processes," Chapter 16, McGraw-Hill, New York (1965).

Rayleigh, Lord, "On the Manufacture and Theory of Diffraction Grating," *Phil. Mag.*, **11**, 196 (1881).

White, E. T., and Beardmore, R. H., "Velocity of Rise of Cylindrical Air Bubbles Through Liquids Contained in Vertical Tubes," *Chem. Eng. Sci.*, **17**, 351 (1962).

Wigley, E., "The Sizing of Large Droplets by Laser Anemometry," *UKAEA Report* AERE-R8771 (1977).

Manuscript received March 3, 1980; revision received June 6, and accepted June 17, 1980.

R & D NOTES

Hydrogen Permeation through Nickel in Gas and Liquid Phase

H. B. GALA, M. KARA,
S. SUNG, S. H. CHIANG,
and
G. E. KLINZING

Chemical and Petroleum Engineering Dept.
University of Pittsburgh
Pittsburgh, PA 15261

Hydrogen has great importance today in the energy conversion and utilization field. The behavior of hydrogen with some metals is indeed unique showing structural decomposition of hydrogen molecule. This unique property of hydrogen can be utilized in developing a device for measuring hydrogen partial pressure, in situ. Nickel is ideally suited for developing such a tool (Gala, 1979). Many workers have studied the motion of

---

0001-1541-81-3386-0160-$02.00. ©The American Institute of Chemical Engineers, 1981.

hydrogen in various metals and measured transport coefficients—permeability and diffusivity in the system (Cotterill, 1961; Smith, 1948). Substantial data are available for these transport coefficients of hydrogen through nickel in literature (Robertson, 1973; Ebisuzaki, et al., 1967; Louthan, et al., 1976; Smithells and Ransley, 1935, 1936; Shcherbakova, 1956; Cermek, 1956; and Yamahawa, 1977). Most of these data are for low-pressure gas-phase conditions. At present, there exist very little data in which permeability of hydrogen in metals is measured at high pressure or in the liquid phase (Louthan et al., 1976; Smithells and Ransley, 1935, 1936; and Shcherbakova, 1956).

A nickel probe, which can measure hydrogen partial pressure/concentration in situ, was developed. This probe was used to measure hydrogen permeability through nickel at high pressures, both in gas as well as liquid phase.

The pressure range of 1 to 12 MPa was investigated and the temperature range of 575 to 770 K was studied.

THEORY

The permeation of hydrogen through nickel can be assumed to take place in the following sequence of steps (Robertson, 1973):

(a) Adsorption of the hydrogen on the nickel entrance surface.

(b) Dissolution of the absorbed hydrogen in atomic form in the nickel:

$$H_2 \rightarrow H + H \text{ or } H_2 \rightarrow 2H^+$$

(c) Diffusion of the atomic hydrogen through the bulk of nickel membrane.

(d) Movement (and/or combination) of the atomic hydrogen to the absorbed state on the exit surface of nickel.

(e) Desorption of the hydrogen molecule from the nickel surface.

Any of the above processes could be the controlling step in the total permeation process. Experiments suggest that generally the surface processes are very fast and the diffusion process is slow (Fischer, 1967). As a result, the transport of hydrogen through the nickel membrane can be treated as one of diffusion-controlled process (step c). Assuming that the Sieverts law (Sievert, 1929) for solubility of hydrogen in metals is valid and applying Fick's law for the case of steady state with small rate of diffusion; the flow rate Q, at which hydrogen will permeate through a membrane of surface area A and thickness x will be given by:

$$Q = \Phi \frac{A}{x} \left(\sqrt{P_1} - \sqrt{P_2} \right) \tag{1}$$

where P_1 is hydrogen partial pressure on high-pressure side and P_2 is that on low-pressure side and Φ is the permeability. Permeability can be expressed as the product of diffusivity and solubility constant as:

$$\Phi = D \cdot K \tag{2}$$

The method commonly used for determining permeability and diffusivity is the "time lag" method (Barrer, 1959). In this present work permeability was determined by measuring the hydrogen flow rate Q directly.

The flow rate of hydrogen through nickel membrane is very small. So, to measure this flow rate a micro-flowmeter was designed. The operation of this meter is described later. For a given membrane of known surface area and thickness, if the hydrogen pressure on both sides of the membrane is maintained constant, permeability can be determined from Eq. 1 by measuring the flow rate Q.

The permeability has an Arrhenius type of dependency on temperature given as:

$$\Phi = \Phi_0 \exp(-E/RT) \tag{3}$$

From a set of permeability data at several experimental temperatures, Φ_0 and E can be determined.

EXPERIMENTAL APPARATUS

The experimental setup for measuring hydrogen permeability through the nickel membrane is sketched schematically in Figure 1. It essentially contains a $10^{-3}m^3$ (1 L) capacity autoclave designed to work up to 35 MPa pressure at 750 K. The nickel probe was installed in the autoclave. The autoclave was equipped with a variable speed magnetically driven agitator, an electrical heater with temperature controller, a thermowell, a cooling coil, and inlet and outlet for gas. The autoclave and the probe were connected to feed section which contained high-pressure hydrogen, nitrogen, and helium gas tanks. Helium and nitrogen were used for purging and leak testing the system. The probe and autoclave were also connected to vent and vacuum pump. All the lines and fittings were rated 75 MPa at room temperature.

The pressure in the probe and the vessel was measured with high-pressure Heise gauges. The autoclave was heated by two heaters and the temperature inside the vessel was measured by a chromel-alumel thermocouple and was controlled within ±0.5% by a proportional controller over a long period of time.

The nickel probe developed for measuring in-situ hydrogen concentration is shown in Figure 2. It consists of a thin nickel bellows of thickness 0.06 to 0.13 mm and an average surface area of $2 \times 10^{-3}m^2$, welded to a 3.2-mm diameter stainless-steel tube at both ends. The steel tube has holes drilled in it so that hydrogen gas permeating through the nickel surface passes through the holes. These probes were subjected to severe mechanical and thermal testing to determine safe operating temperature and pressure range. Thicker probes were able to withstand a pressure difference of 1.5 MPa at 800 K.

The micro-flowmeter designed for the measurement of very small flow rates (of the order of 10^{-10} m^3/s) at high pressure consists of precision glass capillary of 0.5- to 1.0-mm diameter enclosed in a cast-iron housing. The flowmeter was rated 40 MPa. The thick glass capillary contains a very small mercury drop. The hydrogen flow through the system is determined by measuring the time taken for the mercury to travel a known volume. The direction of flow in the flowmeter is controlled by a multiport valve. It can (a) bypass the flowmeter, (b) allow the mercury to travel backward from B to A. The working of flowmeter is explained in Figure 3. One end of the flowmeter was connected to high-pressure tank and the other end to the probe.

Procedure

Before a test run, the system was leak-tested at a pressure higher than the experimental pressure with helium. A very sensitive helium leak detector was used to check all the connections in the system. After making certain that the system was leak-proof, it was vented and evacuated to at least 10^{-4} MPa pressure.

Direct Measurement of Flow Rate. In this set of experiments, the autoclave was pressurized with a known hydrogen pressure P_2 (for runs below 3 MPa, P_2 was kept at zero and the autoclave was pressurized with helium or nitrogen), and heated up to desired temperature level. After a steady temperature was attained, the inside of the probe was opened to a hydrogen storage tank so that a constant pressure P_1 was maintained in the probe. The hydrogen was allowed to permeate through the probe for a few minutes (to ensure a steady state) and then the permeation rate was measured using the flowmeter. Several flowmeter readings were taken for each set by allowing the mercury to flow forward and backward. An average flow rate was computed and was corrected for temperature and pressure to obtain permeation rate Q at normal temperature and pressure conditions. Eq. 1 was then used to calculate the permeability Φ. Data were collected over a range of temperature and an Arrhenius type of equation was fitted to the data.

To study the effect of surface structure on the permeation characteristic of hydrogen, the surface of nickel was sulfided. The nickel probe was sulfided by treating it with benzothiophene dissolved in tetralin in the presence of hydrogen. Several gas-phase runs were conducted with the sulfided probe as outlined above. The data collected were compared with those of the unsulfided probe.

For the liquid-phase runs benzene and tetralin were used, and the same procedure outlined above was followed. The liquid was charged in the autoclave from the liquid feed tank by gravity or by applying vacuum. The liquid was then heated up and the hydrogen was allowed to permeate through the nickel probe.

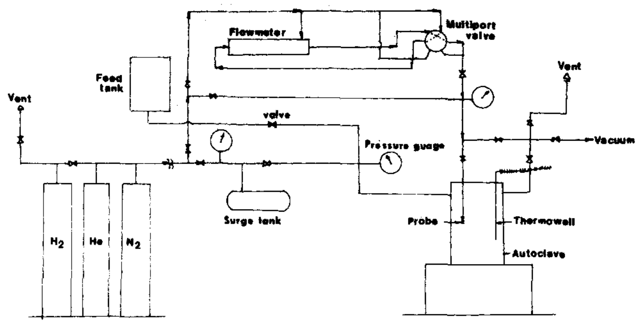
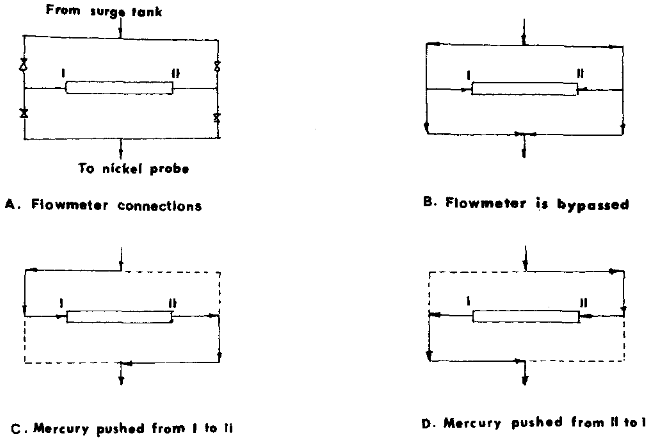


Figure 1. Schematic diagram of experimental setup.



A. Flowmeter connections

B. Flowmeter is bypassed

C. Mercury pushed from I to II

D. Mercury pushed from II to I

Figure 3. Working of micro-flowmeter.

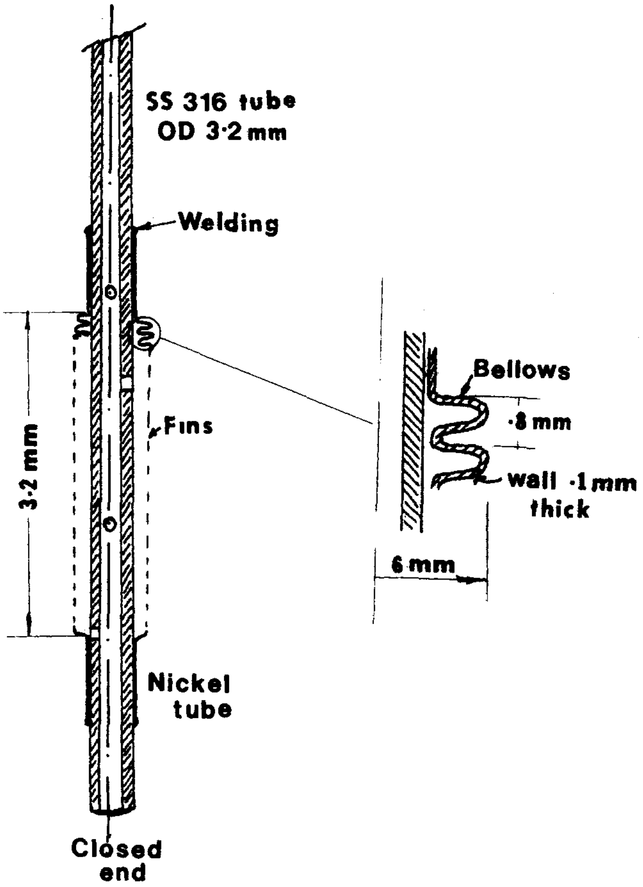


Figure 2. Nickel probe.

RESULTS

Values of permeability Φ were calculated from the data collected using Eq. 1. This data were analyzed statistically by converting Eq. 2 into a linear form. Figure 4 shows a plot of these data with the statistical "best fit." The "best fit" as obtained by the least square analysis of the data is:

$$\Phi = 5.341 \times 10^{-6} \exp(-52210/RT)\ \mathrm{m^3\ (NTP)/m/s/\sqrt{MPa}}$$

Figure 4 also shows the region of 90% confidence level.

The effect of pressure on permeability can be observed by the plot of permeability vs. hydrogen pressure in Figure 5. As the figure indicates, pressure does not have any substantial effect on the permeability. The validity of Sieverts law was checked by making a plot (Figure 6) of flow rate Q vs. the driving force.

DISCUSSION

Up to a pressure of about 12 MPa, no significant effect of pressure on permeability was observed. However, permeability is very strongly dependent on temperature, a 1% variation in temperature can introduce as much as 10% deviation in permeability (Gala, 1979). When the probe was immersed in liquid phase, no significant difference was observed in the rate of permeation compared to the gas phase. The controlling step in the permeation of hydrogen is the diffusion through the metal membrane. Thus, the medium inside or outside the probe does not affect the rate of permeation. Comparison of the order of

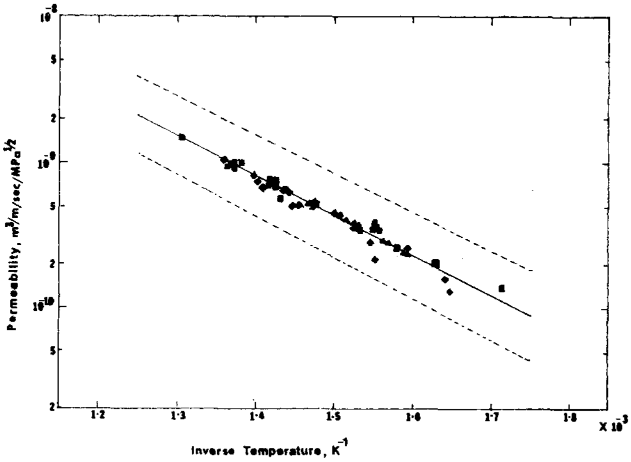


Figure 4. Arrhenius plot for data. ■ Gas-phase data; ▲ Liquid-phase data; ◆ Data with sulfided probe; ---- Region of 90% confidence.

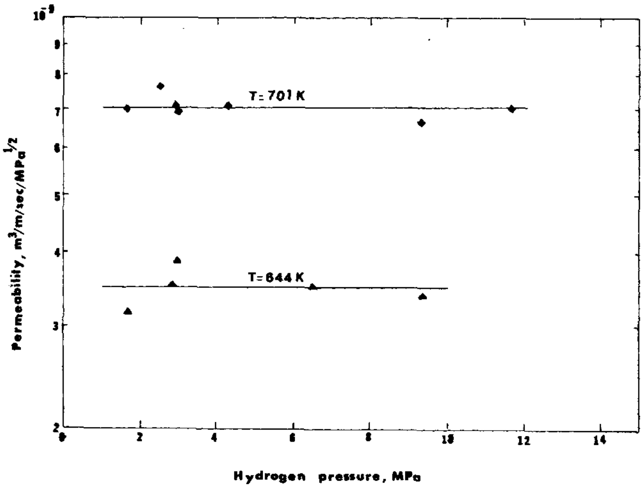


Figure 5. Effect of pressure on permeability.

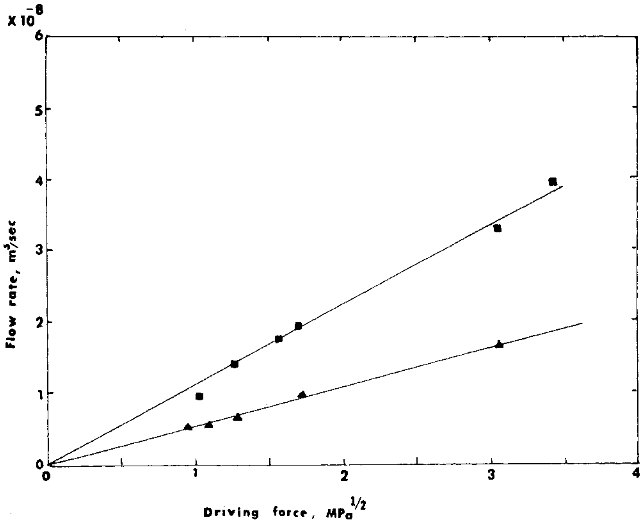


Figure 6. Sieverts law plot. ■ T = 701 K; ▲ T = 644 K.

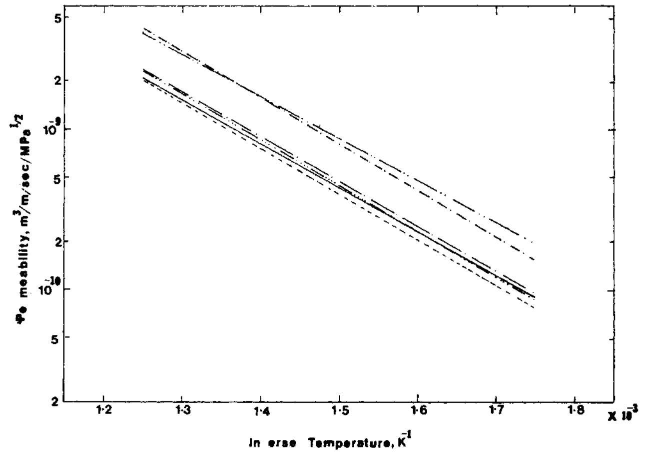


Figure 7. Comparison with literature. —— Present Work; --- Robertson, 1973; -·····-· Robertson's Best Fit, 1973; —·— Shcherbakova, 1956; -·-·- Louthan, et al., 1975; —··—· Smithells, 1935.

magnitude values of gas diffusivity in gas, liquid, and solid also indicate that the hydrogen permeation through the metal is controlling. Fischer (1967) additionally found that the surface processes are much faster than the diffusion process which are also confirmed by our experiments with the sulfided probe.

COMPARISON

Robertson (1973) has compiled the literature data on hydrogen permeability through nickel. The data collected in present work agrees very well with the "best fit" of Robertson and lies well within the envelope of reported data. The comparison of literature data with present work is shown in Figure 7. Relatively very few studies extend up to a pressure range of 10-15 MPa. Shcherbakova (1956) and Smithells (1935, 1936) measured permeability at 10-12 MPa pressure. The present data agree very well with this data. Recent experimental data are also in good agreement with present data (Robertson, 1973).

CONCLUSION

From the present study, it can be concluded that:

A. The nickel probe can be used effectively in measuring in-situ hydrogen partial pressure.

B. The micro-flowmeter could be used to measure very small gas flowrates.

C. Sieverts law for predicting hydrogen solubility is valid up to 12-MPa pressure.

D. Permeability of hydrogen in nickel is independent of pressure.

E. Permeation of hydrogen in nickel is characterized by a slow rate governing diffusion step.

F. The permeability coefficient of hydrogen in nickel over a wide range of temperature and pressure can be estimated by the equation.

$$\Phi = 5.341 \times 10^{-6} \exp(-52210/RT) \text{ m}^3\text{ (NTP)/m/s/}\sqrt{\text{MPa}}$$

ACKNOWLEDGMENT

This work was supported by a grant from the Dept. of Energy.

NOTATION

A = effective surface area of nickel membrane, m^2
E = activation energy, kJ/mol
K = solubility constant, kg·mol/m^3/$\sqrt{\text{MPa}}$
P_1 = hydrogen pressure on high side, MPa
P_2 = hydrogen pressure on low side, MPa
Q = flow rate of hydrogen through nickel, m^3(NTP)/s
R = universal gas constant, 8.312 kJ/kmol/K
T = temperature of gas, K
t = time, s
x = thickness of probe, m

Greek Letters

Φ = permeability, m^3(NTP)/m/s/$\sqrt{\text{MPa}}$
Φ_0 = constant, m^3(NTP)/m/s/$\sqrt{\text{MPa}}$

LITERATURE CITED

Barrer, R. M., "Diffusion In and Through Solids," Cambridge Press, London, England (1951).

Cermek, J., and A. Kufudakis, "Diffusion—Elastic Phenomenon and Diffusivity of Hydrogen in Nickel," *J. of Less Common Metals*, **49**, 309 (1976).

Cotterill, P., *Progress in Material Science*, **9**, 205 (1961).

Ebisuzaki, Y., W. J. Kass, and M. O'Keeffe, "Diffusion and Solubility of Hydrogen in Single Crystals of Nickel and Nickel-Vanadium Alloy," *J. of Chem. Physics*, **46** (4), 1378-1383 (1967).

Fischer, W., "Uber Die Kirctik der Wasserstaff Permeation Durch Nickel," *Naturforschg*, **22 A**, 1581 (1967).

Gala, H. B., "Hydrogen Permeation through Nickel at High Pressures," M. S. Thesis, Univ. of Pittsburgh (1979).

Louthan, Jr., M. R., J. R. Donovan, and J. R. Gaskey, Jr., "Hydrogen Diffusion and Trapping in Nickel," *Senpta Metallurgica*, **23**, 745-749 (1975).

Robertson, W. M., "Hydrogen Permeation, Diffusion and Solution in Nickel," *Z. Metallkde*, 436-443 (1973).

Shcherbakova, A. A., "Diffusion of Hydrogen Through Iron and Through the Binary Alloys of Iron-Chromium and Iron-Nickel at High Pressures and Temperatures," *Zhur. Priklad. Khim.*, **29**, 879-884 (1956).

Sidorenko, V. M., B. F. Kachmar, and N. S. Borisova, "Effect of Stress and Strain on the Diffusion Characteristic of Hydrogen in Metals," *Fiziko-Khim. Mekhan. Mat.*, **g**(5), 14 (1973).

Sieverts, A., (i) "Solution of Gases in Metals," *Z. Elektrochem*, **16**, 701-713 (1911); (ii) "Absorption of Gases by Metals," *Z. Mettalkde*, **21**, 37-46 (1929).

Smith, D. P., *Hydrogen in Metals*, Univ. of Chicago Press, Chicago (1948).

Smithells, C. J., and C. E. Ransley, "The Diffusion of Gases Through Metals," *Proceeding of the Royal Society* (London), **A 150**, 172-197 (1935); ibid, "The Diffusion of Gases through Metals: IV. The Diffusion of Oxygen and Hydrogen through Nickel at Very High Pressures," *Proceeding of the Royal Society* (London), **A 157**, 292-302 (1936).

Yamahawa, K., and F. E. Fujita, "Diffusion of Hydrogen in Hydrogen-Quenched Nickel," *Japanese J. of Applied Physics*, **16**(**10**), 1742 (1977).

Manuscript received January 14, 1980; revision received March 18, and accepted April 7, 1980.