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THE DIFFUSION OF HYDROGEN IN BETA ZIRCONIUM

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William M. Albrecht and W. Douglas Goode, Jr.

Diffusion coefficients for hydrogen in beta zirconium were determined from permeation rates in the range 650 to 850 C. Both the steady-state method, which is dependent upon the hydrogen concentration, and the time-lag method, which is independent of hydrogen concentration, were employed to obtain diffusion data.

Zirconium disks, 0.03 to 0.1 cm thick and varying in hydrogen concentration from 9 to 33 a/o, were used to measure permeation rates. The diffusion coefficients determined by the steady-state and time-lag methods on samples of differing thickness were in agreement. It was concluded that the permeation process was diffusion controlled. The diffusion coefficients were found to be independent of concentration and can be expressed by $D = 6.14 \times 10^4 \exp(-45,900/RT)$.

INTRODUCTION

The diffusion of hydrogen in alpha zirconium has been studied by Schwartz and Mallett⁽¹⁾ and Mallett and Albrecht⁽²⁾. The diffusion of hydrogen in zirconium hydride has been studied by Gulbransen and Andrew⁽³⁾. Bernstein and Cubicciotti⁽⁴⁾ have measured permeation rates of hydrogen through zirconium. However, their results were not reproducible and most of their samples were composed of two or three phases under the conditions of their experiments. They attribute the variation of their results to contamination of their samples.

The purpose of this study was to determine the diffusion coefficients of hydrogen in beta zirconium and the effect of hydrogen concentration on them. Permeation rates were determined with beta-phase zirconium disks having a small hydrogen-concentration gradient across the thickness. The average concentration level was varied in successive experiments at the same temperature.

THEORETICAL CONSIDERATIONS

Diffusion coefficients can be determined from the permeation data by the steady-state method. This is based on a solution of Fick's first law of diffusion⁽⁵⁾. Crank⁽⁶⁾ gives a solution in the form

$$D = F\ell / A(C_1 - C_2), \quad (1)$$

where

D = diffusion coefficient

F = linear permeation rate at steady state

(1) References at end of text.

ℓ = thickness of disk

A = surface area of one face of the disk

C_1, C_2 = respectively, hydrogen concentrations on the upstream and downstream faces of the disk.

It is seen that this method depends upon the hydrogen concentrations at the surfaces of the disk. These concentrations can be regulated by applying controlled pressures of hydrogen gas at the surfaces. Pressure-concentration data can be obtained from equilibria studies of the zirconium-hydrogen system.

Barrer⁽⁷⁾ discusses the possibility that the effective surface concentration during permeation may not be that determined from equilibria studies. Therefore, the time-lag method, which is independent of concentration, was employed to obtain diffusion coefficients for comparison with those obtained by the steady-state method. This method, developed by Barrer⁽⁸⁾, is based on the time lag, L , related to the time required to establish steady-state conditions after permeation is initiated through a sample originally of uniform concentration. The diffusion coefficient is calculated from the relationship

$$D = \ell^2 / 6L. \quad (2)$$

Agreement between the diffusion coefficients obtained by this method and the steady-state method indicates that the experimental surface concentrations are essentially those obtained from equilibrium data.

ZIRCONIUM-HYDROGEN EQUILIBRIUM

Several studies of equilibrium in the zirconium-hydrogen system have been made including the early work of Sieverts and co-workers^(9, 10). Later studies were made by de Boer and Fast⁽¹¹⁾, Hall, Martin, and Rees⁽¹²⁾, Edwards, Levesque, and Cubicciotti⁽¹³⁾, Gulbransen and Andrew⁽¹⁴⁾, and Mallett and Albrecht⁽²⁾. However, these studies either were made with rather impure (high hafnium) zirconium or did not yield sufficient data for the beta phase. Ells and McQuillan⁽¹⁵⁾ have studied the equilibria in the beta phase up to 40 a/o hydrogen, using hafnium-free (0.01 a/o hafnium) zirconium. These data were considered to be the best for use in this study even though the concentration range was limited. The data appear as isotherms in Figure 1, a logarithmic plot of hydrogen concentration in milliliters STP of hydrogen per cubic centimeter of zirconium against equilibrium-hydrogen pressure in millimeters of mercury. The sections of the isotherms above 40 a/o are approximations based on the study of Edwards, et al. ⁽¹³⁾

FIGURE 1. LOGARITHMIC PLOT OF EQUILIBRIA IN THE BETA PHASE IN THE ZIRCONIUM-HYDROGEN SYSTEM⁽¹⁵⁾

EXPERIMENTAL WORK

Materials

Arc-melted iodide zirconium rod was fabricated into sheets approximately 0.1, 0.09, 0.06, and 0.03 cm thick. Disks 2.22 cm in diameter were cut from these sheets. Results of spectrographic, chemical, and vacuum-fusion analyses of the fabricated metal are given in Table 1.

Pure hydrogen was obtained from the thermal decomposition of uranium hydride prepared from dry, tank hydrogen and degreased uranium chips.

Method

A zirconium-disk sample was polished through 240-, 400-, and 600- grit silicon carbide paper. It was then placed in the stainless steel permeation cell, Figure 2, which was designed so that the sample could be sealed between two compression rings 1.27 cm (1/2 in.) in diameter by bolting the two flanged sections together. The cell was then

TABLE 1. ANALYSIS OF IODIDE ZIRCONIUM
FOR DIFFUSION STUDIES

Element	Analysis, ppm
Iron	550
Hafnium	500
Aluminum	200
Molybdenum	200
Silicon	100
Nickel	50
Copper	50
Calcium	50
Lead	30
Chromium	30
Boron	<10
Manganese	<10
Magnesium	<10
Oxygen	330
Nitrogen	10
Hydrogen	30

sealed into the permeation apparatus, shown schematically in Figure 3, and evacuated below 10^{-5} mm of mercury for 16 hr. It was then heated to experimental temperature in a resistance furnace. The temperature of the sample was measured by a platinum-platinum 10 w/o rhodium thermocouple inserted through the downstream section of the cell so that the bead was in contact with the sample. The sample and permeation cell were degassed for at least 1 hr at this temperature.

It is seen in Figure 3 that there is a differential oil manometer and a pressure regulator on each side of the permeation cell. Thus, hydrogen may be delivered to both sides of the permeation cell from the generator and storage system at the desired pressures. Prior to initiating permeation, the sample was allowed to reach equilibrium at the temperature of the experiment and the pressure, p_2 , to be maintained on the downstream face of the sample. Permeation was started by instantaneously raising the pressure on the upstream face of the disk from p_2 to p_1 . The pressures, p_1 and p_2 , were maintained throughout the experiment. The hydrogen which permeated the sample was passed through the pressure regulator and pumped into the calibrated collection volume (Figure 3). It was calculated from the data of Flint⁽¹⁶⁾ that less than 5 per cent of the gas permeating the sample diffused through the stainless steel walls of the cell. No correction was made for this. The pressure of the collected gas, Q , was measured with the McLeod gage at convenient time intervals. The permeation rate, F , was obtained from a plot of Q against time and the time lag, L , was the intercept of the projected linear rate on the axis, $Q = 0$.

Several determinations were made with each zirconium disk. Between determinations the disk was degassed and slowly cooled to room temperature. For the next determination, it was reheated and equilibrated at the new temperature and/or pressure. The disks remained bright and shiny. Analyses before and after use indicated no oxygen contamination during the experiments.

RESULTS AND DISCUSSIONS

Diffusion coefficients for hydrogen in beta zirconium were determined in the range 650 to 850 C using samples with average hydrogen concentrations from 9 to 33 a/o. A typical permeation-rate curve obtained at 700 C with a sample 0.065 cm thick having an average concentration of 17.9 a/o hydrogen is shown in Figure 4. The steady-state permeation rate, $F = 4.65 \times 10^{-3}$ ml per sec, and the time lag, $L = 230$ sec, are indicated. In many of the experiments, one or both of the pressures, p_1 and p_2 , varied during the first few minutes of permeation. The data from these experiments were unsuitable for determining the diffusion coefficient by the time-lag method; however, the steady-state method could be applied to data obtained after the pressures had been stabilized. At 850 C the time lag was too small to be determined accurately.

The experimental conditions and diffusion coefficients are summarized in Table 2. The agreement between the diffusion coefficients obtained by the steady-state and time-lag methods indicates that the use of static equilibrium concentrations is justified. It is seen that there is good agreement between the diffusion coefficients obtained at each temperature except at 650 C. Reproducible data were difficult to obtain at this temperature due to the difficulty in controlling the low pressures required.

FIGURE 2. AXIAL CROSS SECTION OF PERMEATION CELL

FIGURE 3. SCHEMATIC DIAGRAM OF PERMEATION APPARATUS

FIGURE 4. PERMEATION AT 700 C OF HYDROGEN THROUGH A 0.065-cm-THICK BETA ZIRCONIUM DISK WITH AVERAGE HYDROGEN CONCENTRATION OF 17.9 a/o PERCENT

FIGURE 5. TEMPERATURE VARIATION OF DIFFUSION COEFFICIENTS FOR HYDROGEN IN BETA ZIRCONIUM

TABLE 2. SUMMARY OF EXPERIMENTAL CONDITIONS AND DIFFUSION COEFFICIENTS FOR HYDROGEN IN BETA ZIRCONIUM

Temperature, C	Sample Thickness, cm	Average Hydrogen Concentration, a/o	Pressure on Sample, mm of mercury	Diffusion Coefficient, 10 ⁻⁷ cm ² per sec		
				Steady-State Method	Time-Lag Method	
650	0.065	22.4	0.92	0.35	6.1	4.5
650	0.029	27.9	1.07	0.70	17	--
650	0.065	30.7	1.50	0.70	5.2	12
700	0.065	17.9	1.44	0.79	33	31
700	0.029	20.3	1.57	1.13	22	--
700	0.089	25.0	2.07	1.79	32	--
700	0.063	29.8	4.47	1.44	28	28
750	0.063	15.4	2.26	1.49	120	--
750	0.089	21.4	3.82	3.08	140	--
750	0.063	28.6	7.87	4.47	100	95
750	0.029	32.8	8.07	7.77	160	--
800	0.101	9.7	1.98	1.34	400	430
800	0.101	20.4	6.80	6.40	340	--
800	0.063	20.6	8.39	5.21	340	--
800	0.063	27.4	14.5	10.4	280	330
800	0.029	28.7	13.6	13.3	320	--
850	0.085	9.6	3.45	2.63	450	--
850	0.085	20.1	13.3	12.1	710	--
850	0.085	29.1	29.0	28.2	660	--
850	0.065	29.5	30.2	28.6	460	--
850	0.065	29.7	31.1	28.6	470	--

Also it is seen in Table 2 that no orderly variation of the diffusion coefficients with concentration or thickness of sample was found. The variation of the logarithms of the diffusion coefficients with reciprocal temperature is shown in Figure 5. The data can be described by the equation,

$$\text{Log } D = (-10,020 \pm 270)/T(K) + (4.79 \pm 0.28), \quad (3)$$

which was calculated by the least-squares method. Putting Equation (3) in the form

$$D = D_0 \exp (-E/RT), \quad (4)$$

the activation energy, E , is calculated to be 45.9 kcal per g-atom and D_0 is 6.14×10^4 cm² per sec. The entropy of diffusion, ΔS , was calculated from these values by the theory of Wert and Zener^(17, 18) for interstitial diffusion. For the body-centered-cubic lattice

$$D_0 = (1/6) a_0^2 \nu \exp (\Delta S/R), \quad (5)$$

where a_0 is the lattice constant and ν is the frequency of vibration of a solute atom in an interstitial position. The vibrational frequency was approximated from the relationship

$$\nu = [E / (2m \lambda^2)]^{1/2}, \quad (6)$$

where E is the activation energy in ergs per g-atom, m is the mass of a g-atom of the solute, and λ is the distance between interstitial positions ($\lambda = a_0/2$). ΔS was calculated from Equations (5) and (6) to be 30.7 cal/(g-atom)(C). According to theory, this positive value of ΔS is characteristic of interstitial diffusion.

CONCLUSIONS

Diffusion rates of hydrogen in beta zirconium have been determined at 650 to 850 C by permeation techniques using both the steady-state and time-lag methods. Permeation rates were measured with zirconium disks 0.03 to 0.1 cm thick which varied in average hydrogen concentration from 9 to 33 a/o. Since the diffusion coefficients determined by the steady-state and time-lag methods on samples of differing thickness are in agreement, it is concluded that the permeation process was diffusion controlled. Within the limits of experimental error, there was no change in diffusion coefficients with concentration. The diffusion of hydrogen in beta zirconium may be described by the equation

$$D = 6.14 \times 10^4 \exp (-45,900/RT), \quad (7)$$

where the activation energy for the diffusion process is 45.9 ± 1.2 kcal per g-atom. The entropy of diffusion is 30.7 cal/(g-atom)(C) which is consistent with the theory of interstitial diffusion.

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