

# Accurate measurement of hydrogen diffusivity in metals

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(Received 26 September 1983; accepted for publication 6 November 1983)

An accurate resistometric technique for measuring fast diffusion of hydrogen in metals is described. The sample is in the form of a foil having uniform cross section and a length much greater than its width. Samples are electrolytically loaded with hydrogen to about 0.5 atomic percent. Initially the hydrogen is held at uniform concentration in essentially half the length of the foil by the effect of a dc electrotransport current of 2500 A/cm<sup>2</sup> in the other half. After this current is removed, the diffusion of hydrogen into the second half is monitored by its effect on the resistance of a small section of the foil. With this technique a single sample may be reused to make many measurements of  $D$ . The measurement of  $D$  is absolute, and use of a sensitive differential ac measurement yields results for low hydrogen concentrations.

PACS numbers: 66.30.Jt

## INTRODUCTION

Resistance techniques for measuring the diffusivity of hydrogen in metals are ideally suited for measuring large diffusion coefficients ( $D$ ), that is  $D \gtrsim 10^{-6}$  cm<sup>2</sup>/s in samples of convenient size. Here we describe a resistance technique for measuring the diffusivity of hydrogen in metals which results in an accurate *absolute* determination of  $D$ . Although this method has features in common with other resistometric methods,<sup>1,2</sup> it differs in that electrotransport<sup>3</sup> of hydrogen is used to establish the initial hydrogen distribution. The technique described here allows a single sample to be reused for many measurements of  $D$  while retaining the virtue of being simple to instrument. It has been used for measuring diffusivity of both isotopes of hydrogen in vanadium and vanadium-based binary alloys.<sup>4</sup> Other resistance techniques for measuring the diffusivity of hydrogen in metals have been reviewed by Volkl and Alefeld.<sup>5</sup>

This technique is based on the fact that the resistivity of the metal increases linearly with hydrogen concentration for hydrogen to metal atom ratios ( $H/M$ )  $\leq 0.1$ , provided that the solubility limit has not been exceeded. Typically, the resistivity increases about  $1 \mu\Omega$  cm/at. %/H. Thus, measuring resistivity as a function of time provides a convenient means of monitoring the change in hydrogen concentration due to diffusion. In general, a measurement of  $D$  involves establishing a gradient in the hydrogen concentration and then monitoring the flow of hydrogen through the sample by measuring the resistance of a section of the sample as a function of time. From the measured time dependence of the resistivity and a solution to the diffusion equation,  $D$  is determined for the given experimental geometry.

## I. EXPERIMENTAL SAMPLES

The samples used in our study<sup>4,6</sup> were (vanadium alloy) foils with dimensions of 3.50–7.00 cm  $\times$   $\sim 0.1$  cm  $\times$   $\sim 0.01$  cm. In principle, any quasi-one-dimensional rod-like sample could be used. It is necessary only that the sample be of uniform cross section and that its length be precisely known. To facilitate resistance measurements, copper wire leads were soldered to the foils as shown in Fig. 1. In order to make

good electrical contact, it was first necessary to evaporate gold stripes onto the foils where leads were to be soldered since the solder would not wet the bare alloys. Alternatively, electrical leads could be spot welded, although this might introduce unwanted dislocations into the sample material. In addition, an unhydrogenated comparison sample of identical size was prepared with leads attached in the same fashion. Hydrogen was introduced into the foils electrolytically after the leads were attached. The electrolyte used was 1.2 N H<sub>2</sub>SO<sub>4</sub> solution. The charging was stopped when the resistivity increase due to hydrogen indicated a total hydrogen concentration of 0.3–1.0 at. %. Typical charging times were several minutes.

## II. MEASUREMENT OF THE DIFFUSION COEFFICIENT

The hydrogen concentration profile at the beginning of a diffusion measurement is shown in Fig. 2. This profile is set up by passing a large dc current ( $\sim 2000$  A/cm<sup>2</sup> or  $\sim 2$  A in

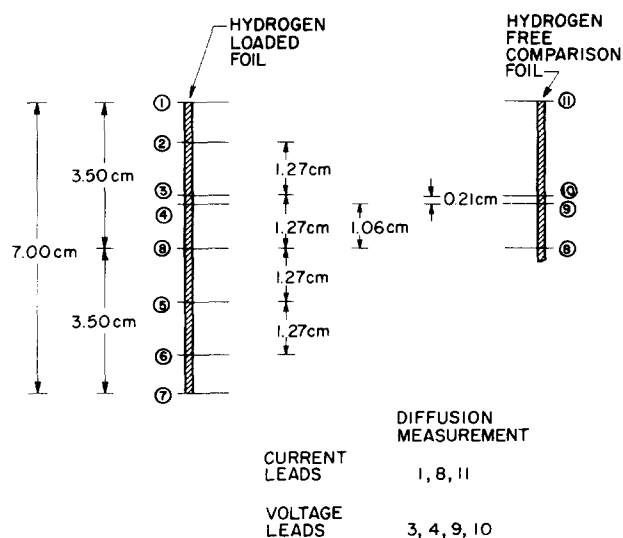


FIG. 1. Geometry of leads for diffusion measurements of metal foil samples. The numbering of the leads indicates which leads were used in diffusion measurements (see text).

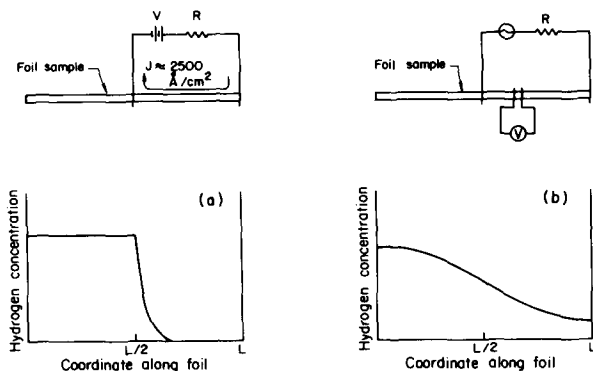


FIG. 2. Measurement of diffusion of hydrogen in metal foils. (a) Initial configuration is attained by sweeping to the left half of foil using electrotransport. (b) Diffusion of hydrogen is monitored with ac current after electrotransport current is switched off.

our samples) through one-half of the sample and thus sweeping nearly all the hydrogen to the other half by means of electrotransport. Electrotransport of hydrogen along the length of the sample can be described by the equation<sup>7</sup>

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} + \mu e Z^* E(x) \frac{\partial c}{\partial x}, \quad (1)$$

where  $c(x, t)$  is the hydrogen concentration along the foil,  $\mu$  the hydrogen mobility,  $e$  the (positive) electronic charge,  $Z^*$  the effective valency of the mobile hydrogen,  $E(x)$  the applied electric field, and  $x$  the coordinate along the length of the foil. For a sample of length  $L$  the electrotransport electric field is

$$E(x) = \begin{cases} 0 & \text{if } x < L/2 \\ E & \text{if } x \geq L/2 \end{cases} \quad (2)$$

From Eqs. (1) and (2), the steady-state hydrogen concentration is found to be

$$c(x) = c_0 \quad \text{for } x < L/2, \quad (3)$$

$$c(x) = c_0 \exp - (x - L/2)/\lambda \quad \text{for } x \geq L/2,$$

where  $\lambda = f k_B T / e Z^* E$  and  $f \equiv D / k_B T \mu$  ( $f \approx 1$  for  $H/M \leq 0.02$ ). Typically, in our experiments  $\lambda \approx 0.3$  cm. In general, the time required to sweep the hydrogen out of the right side ( $x > L/2$ ) of the sample is much less than the time required for the left side ( $x < L/2$ ) to reach a uniform concentration. Therefore, it is the latter time which determines how long it takes for the sample to reach the starting concentration profile. This time is approximately  $L^2/4D$ .

Equation 3 gives the initial condition for a diffusion measurement. Once this condition is attained, the dc electrotransport current is turned off, and the hydrogen begins to diffuse to the right half of the sample (Fig. 2). The diffusion of the hydrogen is followed by monitoring the changing resistance of a point approximately  $L/6$  to the right of the center of the sample as hydrogen diffuses through this region. The resistance increase due to hydrogen diffusion is measured (see Fig. 3) by passing an alternating sinusoidal current ( $\sim 50$  mA) through a hydrogen-loaded foil (leads 1 and 8 in Fig. 1) and through a hydrogen-free comparison foil (leads 8 and 11 in Fig. 1). Transformers were used to subtract the voltage for the hydrogen-free comparison foil (leads 9 and 10 in Fig. 1)

from the voltage for the hydrogen-loaded foil (leads 3 and 4). A variable capacitor and potentiometer on the secondary of each of the signal transformers serve as fine phase and amplitude adjustments, respectively, so that the signals from the two samples can be precisely balanced at the beginning of a diffusion measurement. The differential output from the transformers is measured by a lock-in amplifier whose output is digitized and recorded by a microcomputer. In our experiments approximately 400 to 800 points were taken over the course of a measurement which lasted from 1 to 7 days, depending on the diffusion coefficient of the hydrogen.

The measurements of the resistance were sensitive to changes in hydrogen concentration of approximately 10 at. ppm. Our sensitivity was limited primarily by the resolution of our A/D converter. One ought to be able to improve on the sensitivity by a factor of 10 or more.

In order to minimize changes in resistance due to temperature drifts, the sample and comparison foils were placed in close proximity in a well-stirred oil bath whose long-term temperature stability was better than 0.01 K.

The time development of the hydrogen concentration is governed by the diffusion equation

$$\frac{\partial c}{\partial t} = D \nabla^2 c \quad (4)$$

subject to the condition that there is no hydrogen flux through the surfaces or ends of the sample. A sample may be

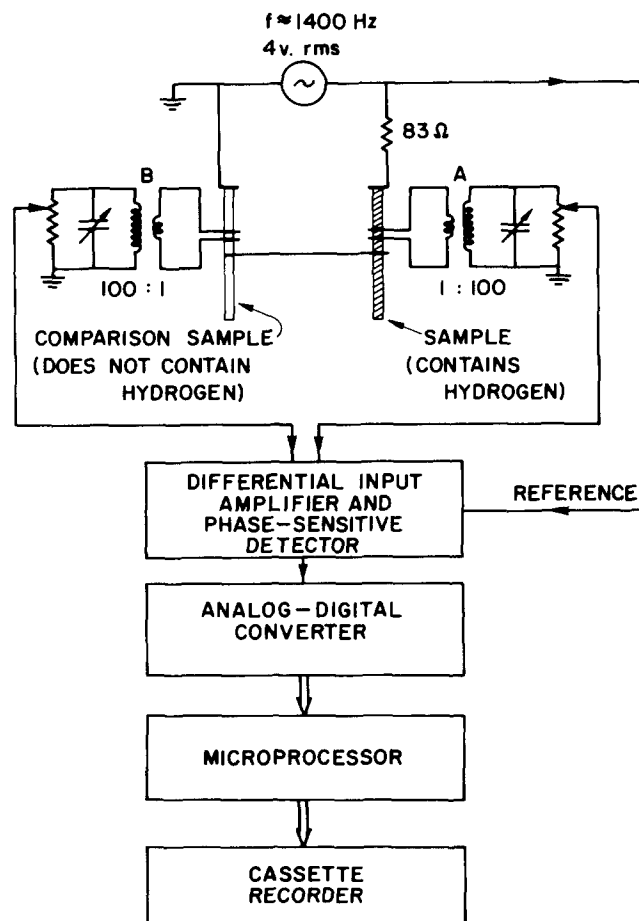


FIG. 3. Schematic/block diagram of the circuit for the measurement of the diffusion coefficient of hydrogen in metal foils. A and B are transformers (Ithaco, Inc., No. B-8810P1).

coated with a hydrogen impermeable lacquer to prevent the flow of hydrogen in or out of the sample. In our experience with vanadium alloys, no such coating was necessary due to a surface oxide which forms naturally. Carslaw and Jaeger<sup>8</sup> give the solution to the diffusion equation using the above boundary conditions for any initial hydrogen concentration profile. For the initial condition specified in Eq. (3), the solution is

$$\frac{c(x, t)}{c_0} = \frac{1}{2} + \frac{1 - e^{-S/2}}{s} + \sum_{n=1}^{\infty} g(n, S) e^{-n^2 \pi^2 D t / L^2} \cos \frac{n \pi x}{L}, \quad (5)$$

where

$$g(n, S) = \sin \frac{n \pi}{2} + \frac{S [\cos(n \pi / 2) - (-1)^n e^{-S/2}] - n \sin(n \pi / 2)}{S^2 + n^2 \pi^2}, \quad (6)$$

and  $S = \lambda / L$ .

Figure 4 shows data from a typical experiment with a fit to Eq. (5). A least-squares fitting routine (CURFIT) from Bevington<sup>9</sup> was used. Three fitting parameters were required: (1) the diffusion coefficient  $D$ , (2) the base line corresponding to the zero hydrogen concentration of the foil, and (3) the asymptotic value of the sample resistance difference as  $t \rightarrow \infty$ . A fourth parameter,  $\lambda$ , needed for the fit was independently obtained from electrotransport measurements in our experiments. The data were also fit with  $\lambda$  as a fourth fitting parameter. The values of  $D$  obtained from three- and four-parameter fits never differed from each other by more than a few percent. An important feature of the fit of the diffusion data is the relative insensitivity of the fitted value of  $D$  to the measured value of  $\lambda$ . Analysis of simulated data shows that a variation of 10% in the supplied value of  $\lambda$  results in less than a 3% change in the fitted value of  $D$  for  $\lambda / L \approx 0.1$ . The same analysis reveals that the fitted value of  $D$  is even less sensitive to variations in  $\lambda$  as  $\lambda$  approaches zero.

It should be emphasized that the data shown in Fig. 4 are not our "best" data. In our "best" measurements of  $D$ , the experimental data could not be distinguished from the fit in a plot like Fig. 4. The shorter the total time of a run, the better the data tended to be. We found that it was especially important to minimize noise from less than perfect solder and switch contacts in order to obtain the best data.

### III. DISCUSSION

The advantages of the resistance technique described in this paper arise from its following characteristics: The use of electrotransport to set up the initial concentration gradient allows a single sample to be reused for many measurements of  $D$  and provides the well-characterized initial hydrogen concentration distribution necessary for an accurate solution to the diffusion equation. The use of an ac technique to measure the resistance avoids problems arising from electrotransport of hydrogen inherent in other resistance techniques. The ac technique also provides a convenient method

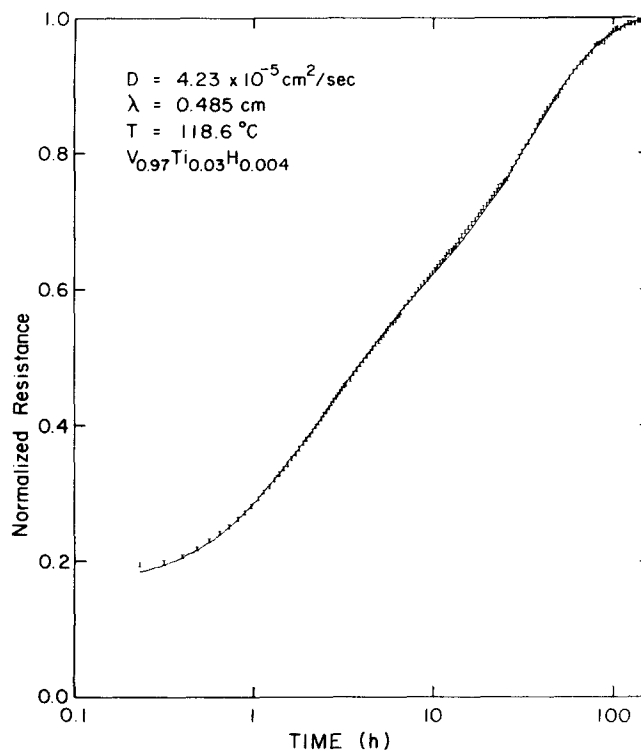


FIG. 4. Typical data from a diffusion measurement. Solid line is obtained from least-squares fit to Eq. 5. The data and fit have been normalized so that the base line and asymptotic values of the resistance differences determined from the least-squares fit are 0 and 1, respectively.

for subtracting off the large "base line" resistance of the bare host metal through the use of transformers. Thus, one measures directly only that resistance arising from the diffusion of hydrogen. Finally, the ac technique allows one to use phase-sensitive detection, thus greatly enhancing the signal-to-noise ratio of the resistance measurements.

### ACKNOWLEDGMENTS

Supported by the National Science Foundation through the Cornell University Materials Science Center, Grant DMR-79-24-008-A03.

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