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ELECTROCHEMICAL DETERMINATION OF HYDROGEN IN STEEL

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ABSTRACT

The electrochemical measurement of the permeation rate of hydrogen through metal foils consists of charging of the metal with hydrogen on one side of the foil and removal of hydrogen by electrochemistry. The hydrogen is present on the surface. The hydrogen diffusion coefficient can be determined by mathematical analysis of the time dependence of the oxidation current. This electrochemical technique can also be used to determine the hydrogen concentration in metals. For this purpose, a portable "barnacle cell" is placed on the metal to be analyzed and a hydrogen concentration gradient is produced by oxidation of all hydrogen atoms which reach the surface. Under a contract with the Naval Air Development Center, a portable "barnacle cell" system - so-called because of its magnetic attachment to steel surfaces - is developed for field use such as determination of hydrogen concentration in aircraft landing gears. The system consists of two parts: the measuring cell in a cylindrical magnet (1.5 inch diameter) and the electronic system which allows recording of the permeation current-time trace and integration of this trace over pre-set time intervals.

The electrochemical permeation method, which was first described by Devanathan and Stachurski (1,2) has been used to determine the diffusion coefficient D and the concentration C0 of hydrogen in iron and steels and to a lesser extent also in other metals. In this method, hydrogen is produced on one side of a metal foil either as the result of the corrosion reaction in acids or by application of a cathodic current. On the other side of the foil, hydrogen which has diffused through the metal is removed by application of an anodic constant potential which leads to oxidation of hydrogen to water. The measurement is carried out in an alkaline solution in which iron is passive and the background current due to iron oxidation is very low.

A modification of the permeation method is the technique which is used in the "barnacle cell" (3,4), so-called because of its magnetic attachment to steel surfaces. With this technique use is made only of the oxidation process to determine the hydrogen concentration in steels. Under contract with the Naval Air Development Center (NADC) a portable barnacle cell system is developed for field use such as determination of the hydrogen concentration in plated steel parts, landing gears, etc. The cell system is developed at the Science Center, Rockwell International, while the electronic measurement system is being designed and fabricated at the Chemistry Department of Portland State University. Three prototypes of the combined system will be delivered to NADC in September 1978.

The permeation method is described in Fig. 1. The diffusion equations, Eqs. 1 and 2, are solved for the electrochemically controlled boundary conditions:

\[ X = 0, \ t \geq 0, \ \phi = 0 \]

\[ X = L, \ t \geq 0, \ \phi = 0 \]

\[ 0 < X < L, \ t < 0, \ \phi = 0 \]

Concentration contours for different times are also shown in Fig. 1 (5). Eqs. 1 and 2 can be solved by a Laplace transformation or a Fourier method. Figure 2 shows a comparison of experimentally obtained data for Armco iron with the build-up transients predicted by the two methods (6).

The diffusion coefficient D and the hydrogen concentration C0 can be determined from the permeation transient (1) as shown in Fig. 3. The sensitivity of the electrochemical method exceeds that of conventional techniques significantly.

For the barnacle cell method Eqs. 1 and 2 are solved with the boundary conditions:

\[ X = 0, \ t \geq 0, \ \phi = 0 \]

\[ X = L, \ t \geq 0, \ \phi = 0 \]

\[ 0 < X < L, \ t \geq 0, \ \phi = 0 \]

Concentration profiles for different test periods are shown in Fig. 4 (3). For the conditions of Fig. 4:

\[ J = F \ C_0 \left( \frac{D}{\pi t} \right)^{1/2} \]

which holds for \[ L^2 < 4t \], i.e., \[ t_{\text{max}} = \frac{L^2}{4D} \]. For 4340 steel (L = 1 mm, D = 2.5 \times 10^{-7} \text{ cm}^2/\text{sec}) \[ t_{\text{max}} \approx 10^4 \text{ sec} \].

The barnacle cell system to be developed under contract is shown in Fig. 5. The cell is attached to the sample and the hydrogen oxidation current is flowing between the steel and Ni/NiO driving electrode. Details of the cell and measuring system are shown in Fig. 6 and 7. The electrolyte (0.2 N NaOH) is contained in a sponge which provides electrical contact between the sample and the Ni/NiO counter electrode. The Ni electrode is used to check whether sufficient electrolyte is contained in the cell. The measuring system contains provisions to monitor the hydrogen oxidation current and to integrate the current-time trace. The current is displayed after a pre-set time interval, the start and the
interval of integration are preset, the total
coulombs are used to calculate the hydrogen con­
ccentration for a given diffusion coefficient.

Figure 8 shows some experimental results ob­
tained with the barnacle cell. In a log current­log time plot the points for charged specimens
fall on a straight line with the theoretical slope
of -0.5, while samples which had not been charged
follow a line with a slope of -1 which presumably
reflects the passivation characteristics of the
steel surface. The average hydrogen concentration
of the charged samples is about 0.32 ppm.

Some applications of the technique are listed
in the last figure which also shows the barnacle
cell attached to a steel tensile sample which had
been charged and Cd plated at NADC to determine
the relationship between hydrogen concentration
and failure characteristic as a function of ap­
pied stress.

ACKNOWLEDGEMENT

This work was performed under contract
N62269-77-C-0351 with the Naval Air Development
Center. The hydrogen permeation experiments were
carried out by S. L. Jeanjaquet and C. S. Tsai.

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• TWO METHODS OF SOLUTION OF EQUATIONS (1) - (2)

• LAPLACE TRANSFORM METHOD

VALID FOR SHORT TIMES (0 < \tau < 0.5)

\[
\frac{J}{J_\infty} = \frac{2}{\sqrt{\pi \tau}} \exp\left[\frac{1}{4\tau}\right], \quad \tau = \frac{Dt}{L^2}
\]

• FOURIER METHOD

VALID FOR LONGER TIMES (\tau > 0.15)

\[
\frac{J}{J_\infty} = 1 - 2 \exp\left[-\pi^2 \tau\right]
\]

Fig. 1 Permeation method; concentration contours
for progressive hydrogen diffusion.

Fig. 2 Comparison of experimental data (x) with
the theoretically predicted build up trans­
ients (-) and (---).
II. HYDROGEN EXTRACTION METHOD ("BARNACLE CELL")

- OUTDIFFUSION OF RESIDUAL HYDROGEN IN STEEL MEASURED IN ELECTROCHEMICAL CELL

- MEASUREMENT AND ANALYSIS OF EXTRACTION CURRENT

- SOLUTION OF EQUATIONS (1) AND (2)

\[
\frac{J}{2F} = C_0 \left( \frac{D}{x} \right)^{\frac{1}{2}} \left[ 1 - e^{-\frac{L^2}{Dx}} + e^{-4L^2/Dx} + \ldots \right]
\]

for \( e^{-L^2/Dx} \ll 1 \cdot \frac{J}{2F} = C_0 \left( \frac{D}{x} \right)^{\frac{1}{2}} \)

Fig. 3 Determination of \( D \) and \( C_0 \) from permeation current.

Fig. 4 Hydrogen extraction method "barnacle cell."

Fig. 5 Barnacle electrode principle.
a) CELL HOUSING

CYLINDRICAL MAGNET, 2" OD, 1-1/8" ID

REFERENCE ELECTRODE

NI ROD (PRESS FIT)

NUTS

SILICONE RUBBER GASKET

EPoxy

SLEEVE

KELF OR POLYETHYLENE

COUNTER ELECTRODE

NI ROD

O-RING

NI MESH

SPRING LOADED CONTACT ID

CYLINDRICAL SPONGE

Fig. 6 Basic design for test cell.

Fig. 7 Panel layout of measuring system.

- TESTING OF DIFFERENT HEATS OF STEEL
- FIELD USE (LANDING GEARS, ETC.)
- PLATING OPERATIONS (H₂ CODEPOSITION, BAKE-OUT EFFICIENCY)
- EMBRITTLEMENT STUDIES

Fig. 8 Experimental results on 4130 steel.

Fig. 9 Applications of barnacle cell.