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Hydrostatic pressure effects on hydrogen permeation in A514 steel during galvanostatic hydrogen charging

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ABSTRACT

A514 offshore structural steel was exposed to hydrostatic pressure ranging from 0.1 to 40 MPa to examine hydrogen permeation during galvanostatic hydrogen charging. Hydrostatic pressure decreases the energy barrier for hydrogen absorption and desorption, while increasing hydrogen adsorption. These effects are induced by both steady-state current density and the apparent diffusivity slight increase with hydrostatic pressure. Taking surface effect of hydrogen permeation into account, the intrinsic diffusivity of $(3.2 \pm 0.04) \times 10^{-6}$ cm^2/s is obtained, which is independent of the hydrostatic pressure.

1. Introduction

Duplex stainless steel is widely used in deep sea engineering due to its combination of high strength and high resistance to pitting corrosion and chloride stress corrosion cracking. However, hydrogen induced-cracking (HIC) has been observed in duplex steel pipes when submerged in deep sea environment. Taylor et al. reported that HIC occurred in super duplex hub forging containing welded pipe connection in the BP Amoco Foinaven Field after only 6 months of service [1]. Hydrogen damage can be caused by both metal structure [2–5] and environmental factors [6,7]. The cathodic protection potential is an important factor of hydrogen damage. Woollin et al. [8] and Du [9] observed that the sensitivity of the HIC increased as the cathodic protection potential decreased, based on the constant load, pre-cracked bending and the slow strain rate tests under different cathodic protection potentials. Olsen et al. proved that hydrostatic pressure could cause a significant increase in hydrogen concentration of super martensitic stainless and duplex stainless steels when immersed in 3.5% NaCl electrolyte with aluminium anodes, which is the reason why HIC occurs in deep sea environment [10]. Thus, studying the mechanism of hydrogen diffusion in metal under different hydrostatic pressure is very important for simulating the hydrostatic pressure effects on hydrogen permeation in metals.

Experiments on hydrogen permeation under hydrostatic pressure have been carried out since 1966. Woodward et al. measured hydrogen permeation in high strength steel under different hydrostatic pressures with potentiostatic hydrogen charging. They found that hydrogen permeation rate was considerably higher at 100 bar than at 1 bar [11]. Similar results were obtained in the Nanis's experiment, where diffusivity remained the same for different hydrostatic pressures [12]. However, Smirnova et al. found that permeation rates for the UNS S4 1000 stainless steel were the same at 1–100 bar when electrolyte at the entry side was stirred [13]. Blundy and Sheer also found that when the electrolyte at the entry side was stirred, the permeation rate for different hydrostatic pressures was the same. They hypothesized that the permeation rate increased with the partial pressure of hydrogen at the entry side and that the hydrostatic pressure did not directly affect the permeation rate [14,15].

Mentioned studies of hydrostatic pressure effects on hydrogen permeation used the classic model to fit the experimental data [11–15], which only considered hydrogen diffusion in the bulk, while surface effects have not been taken into account. Hydrogen solubility in electrolyte increases with hydrostatic pressure [16]. For 10 MPa hydrostatic pressure, hydrogen produced by hydrogen evolution reaction during 1 h with 5 mA/cm^2 hydrogen charging current density completely dissolved in the electrolyte and gathered near the entry side of the membrane, which could restrain adsorbed hydrogen atoms combining into H_2 molecules. It is reasonable to assume that this phenomenon increases the amount of adsorbed hydrogen atoms. Thus, higher hydrostatic pressure causes

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greater subsurface coverage of hydrogen beneath the entry side, induced by the steady-state current density increase with hydrostatic pressure.

The purpose of this work is to quantify the influence of surface hydrogen absorption and desorption on hydrogen diffusivity under different hydrostatic pressure. The effects of the hydrostatic pressure, membrane thickness and Ni coating on hydrogen permeation behaviour were characterized. Taking surface effects of hydrogen permeation into account, the intrinsic diffusivity is obtained, which is independent of the hydrostatic pressure.

2. Hydrogen permeation theories

The Devanathan and Stachurski double cell electrochemical permeation model [17] is the classic model used to study hydrogen diffusion in metals, which is based on the Fick's second law:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \tag{1}$$

In the classic hydrogen permeation model, permeation current build-up transient $J = f(t)$ is recorded when constant potential or constant current is applied at the entry side. In most cases, hydrogen exit side is coated with a thin palladium or nickel layer to achieve full oxidation of hydrogen. It is generally assumed that the diffusion process of hydrogen into the bulk metal is a rate-determining step and that the output concentration is zero. Here, ideal hydrogen permeation boundary conditions can be given by:

$$t = 0, C(x, 0) = 0$$

$$t > 0, C(0, t) = C_0, C(L, t) = 0 \tag{2}$$

By solving the Fick's second law for ideal hydrogen permeation boundary conditions, one arrives at:

$$\frac{J}{J_\infty} = \frac{2L}{\sqrt{\pi D t}} \sum_{n=0}^{\infty} \exp\left(-\frac{(2n+1)^2 L^2}{4Dt}\right) \tag{3}$$

Here, J is the measured permeation rate at time t, J_∞ is the steady-state permeation rate ($t \to \infty$), D is the diffusivity, and L is the specimen thickness.

Classic model is most widely used in hydrogen permeation to obtain diffusivity. However, many researchers have observed that there is scatter of several orders of magnitude in the evaluation of iron diffusivity using the classic model when the membrane thickness is varied [17–19]. This is due to hydrogen trapping in metal defects, which can contribute to discrepancies in the evaluation of the diffusion coefficient [20–22]. Moreover, surface effects are present at the entry side, limiting the permeation rate. The surface effect is related to the specimen thickness in the double cell electrochemical permeation experiments. This relationship has been the subject of many studies [18,23–26] with increasingly lower apparent hydrogen diffusivity obtained for iron and steel membranes of progressively decreasing thickness. Wach et al. [23] claimed that the formation of a barrier at the entry side of the membranes induced an error in the diffusivity values. Equivalent thickness should be considered to correct this value.

To study the surface effect on hydrogen permeation, Wang [27] put forward a model for hydrogen permeation by charging with hydrogen gas, which considered hydrogen adsorption and desorption, to illustrate the deviation of the Siverts' law under low hydrogen pressure. Based on the Wang's model, thermodynamic model for hydrogen permeation was proposed by Zhang et al. to evaluate hydrogen diffusivity, considering both absorption and desorption processes [18]. From the Wang's model, the continuity of the flux at the entry side requires:

$$k_1^+ P_1 - k_1^- C = -D\frac{\partial C}{\partial x}, x = 0 \tag{4}$$

Here, $k_1{}^+$ and $k_1{}^-$ are the rate parameters for hydrogen adsorption and desorption reactions, respectively. The variable P_1 is hydrogen pressure in the gas phase. The variable C is hydrogen concentration.

In the same way, boundary conditions at the exit side are given by:

$$k_2^- C - k_2^+ P_2 = -D\frac{\partial C}{\partial x}, x = L \tag{5}$$

Here, $k_2{}^+$ and $k_2{}^-$ are rate parameters for hydrogen adsorption and desorption reactions, respectively. The variable P_2 is hydrogen pressure in the gas phase. Generally, a membrane has the same energy barrier at both sides. Therefore, for simplicity, Zhang et al. assumed that $k_1{}^- = k_2{}^- = k$, which means that the desorption rate depends on the surface conditions, and that $k_1{}^+ P_1 = k_\mathrm{p}$, which is the absorption parameter. It denotes the forward flux of hydrogen from the gas phase into the sample at the entry side and therefore is related to gas pressure or charging current density in electrochemical tests. Usually, the value of $P_2 = 0$ is used in an electrochemical permeation test.

With the boundary conditions mentioned above, an analytical solution of the Fick's second law is:

$$C = -\frac{k_p}{2D + kL}x + \frac{k_p(D + kL)}{2kD + k^2 L} - \sum_{m=1}^{\infty} A_m e^{-D\lambda_m^2 t}\left[D\lambda_m \cos(\lambda_m x) + k\sin(\lambda_m x)\right]$$

$$A_m = \frac{2k_p}{\lambda_m\left[\left(D^2\lambda_m^2 + k^2\right)L + 2kD\right]} \tag{6}$$

Both diffusivity and desorption rates are evaluated by fitting the entire normalized permeation curve with the following equation:

$$\frac{J}{J_\infty} = 1 + 2(2D + kL)\sum_{m=1}^{\infty}\frac{\left[k\cos(\lambda_m L) - D\lambda_m \sin(\lambda_m L)\right]e^{-D\lambda_m t}}{\left[\left(D^2\lambda_m^2 + k^2\right)L + 2kD\right]} \tag{7}$$

where λ_m is the mth positive root of $\tan(\lambda_m L) = \frac{2kD\lambda_m}{D^2\lambda_m^2 - k^2}$.

The drift velocity through the surface, V_s, and drift velocity in the bulk, V_b, are introduced as:

$$V_s = k, \quad V_b = \frac{D}{L}. \tag{8}$$

Then, the permeation rate at steady state J_∞ can be expressed in terms of the ratio of the drift velocities and the absorption parameter, k_p:

$$J_\infty = \frac{k_p}{2 + V_s/V_b} \tag{9}$$

After evaluating the diffusivity and the desorption rate, the absorption parameter is calculated using Eq. (9). Then, the permeation concentration C_0 is determined from:

$$C_0 = \frac{k_p}{k} \tag{10}$$

Finally, the concentrations at the entry and exit sides for steady state can be evaluated using the following equations:

$$\frac{C_{entry}}{C_0} = \frac{1 + V_s/V_b}{2 + V_s/V_b}, \quad \frac{C_{exit}}{C_0} = \frac{1}{2 + V_s/V_b} \tag{11}$$

Since the absorption, desorption and diffusion are all expressed in the above model, it is possible to measure the effects of hydrostatic pressure on these reactions using the Zhang's model.