Int. J. Electrochem. Sci., 12 **(2017)** 8337 – 8344, doi: 10.20964/2017.09.41

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

A method on hydrogen permeation measurement through steel under constant tensile stress

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Received: 29 March 2017 / *Accepted:* 6 July 2017 / *Published:* 13 August 2017

Hydrogen permeation behavior was studied by many researchers, uniaxial tensile stress may affect the behavior due to the deformation of specimen. However, less study focused on hydrogen permeation behavior during Slow Strain Rate Test (SSRT). In order to clarify elastic and plastic deformation effect on hydrogen permeation, hydrogen permeation behavior was measured by D-S double cell during SSRT in this study. The results show that the background current density increases in elastic deformation range during SSRT due to the damage of thin Ni coating. Hydrogen permeation current density increases slowly in elastic deformation range and decrease quickly in plastic range. The main reason of Hydrogen permeation current density decrease is trapping effect of dislocations that was formed in plastic deformation. Hydrogen permeation current density was affected by the competition mechanism between dislocation trapping and dislocation transport of hydrogen.

Keywords: hydrogen permeation measurement, SSRT, elastic deformation, plastic deformation

1. INTRODUCTION

Hydrogen entry into steel has a devastating effect on strength, ductility, and resulting in brittle failure, including hydrogen induced cracking (HIC) and stress corrosion cracking (SCC) [1-4]. Hence hydrogen permeation into steel has been widely studied by many methods [5-9].

The hydrogen permeation into steel has been measured usually by Devanathan–Stachurski cell [5]. This method performed by plating palladium (Pd) or nickel (Ni) on side of steel (the hydrogen exit side). The thin coating layer on the surface improves the hydrogen oxidation, and a stable hydrogen permeation current density can be easily measured [10–12]. While metals are deformed, trapping and transport by dislocation formed a competition mechanism. Some researchers believe that under externally applied stress, the stability of the coating layer can affect the reliability of hydrogen

permeation test, since the stability of the coating film changes with the elongation of the steel substrate. The hydrogen permeation current density of a Cr–Mo steel (YS = 496 MPa) was measured by Kurkela [9]. They reported hydrogen permeation current increased while the Pd coating film was stretched. Although valuable information about the effect of applied stress on hydrogen permeation was reported, they did not explain clearly whether the decrease in the permeation current under plastic load was due to the trapping of hydrogen by dislocations. Brass and Chene [13] proposed a hydrogen permeation test without Pd coating layer and reported a very low permeation current density. Sung Jin Kim [12] developed a modified hydrogen permeation technique. Instead of coating the Pd layer on the metal surface before applying loading, however, before Pd coating, the tensile loading was applied, the Pd coating deformation can be completely eliminated. Hydrogen permeation behavior was studied by many researchers, uniaxial tensile stress may affect the behavior due to the deformation of specimen. However, less study focused on hydrogen permeation behavior during Slow Strain Rate Test (SSRT).

In this study, D-S cell was used to measure the Hydrogen permeation current density during the whole elastic and plastic deformation of SSRT. The effect of the Ni coating layer deformation on background current density was discussed, and the effect of coating film deformation on hydrogen permeation behavior of pipeline steel was investigated in simulated seawater.

2. EXPERIMENTAL

2.1 Materials and specimens

Commercial X80 pipeline steel was used for the study and its yield strength σ is 398 MPa and ultimate tensile strength σ_b is 406 MPa. 10 mm in diameter cylindrical specimens was used as working electrode, the height is 45 mm and thickness is 0.3 mm, a thin layer of Ni was coated in the inside of the specimen. The outer of the specimen was used as the hydrogen entry side. 250 g L^{-1} $NiSO_4.6H_2O$, 45 g L^{-1} $NiCl_2.6H_2O$ and 40 g L^{-1} H_3BO_3 solution was used, the electroplate current density is -3.0 mA cm^{-2}, the coating time is 3 minutes [14]. The specimens were cleaned by alcohol, acetone by ultrasonic bath, and dried with cold air before the test.

2.2 Experimental methods and experimental set-up

Figure 1 shows the experimental setup. The inside of the specimen was filled with 0.1 mol L^{-1} NaOH. The counter electrode is Pt and the reference electrode is Ir. The specimen was polarized potentiostatically before test at 50 mV vs Ir electrode in NaOH until the background current density was lower than 0.1 uA cm^{-2}. The test temperature was 298 K. It is found that the hydrogen permeation current is related to the strain rate [15,16].

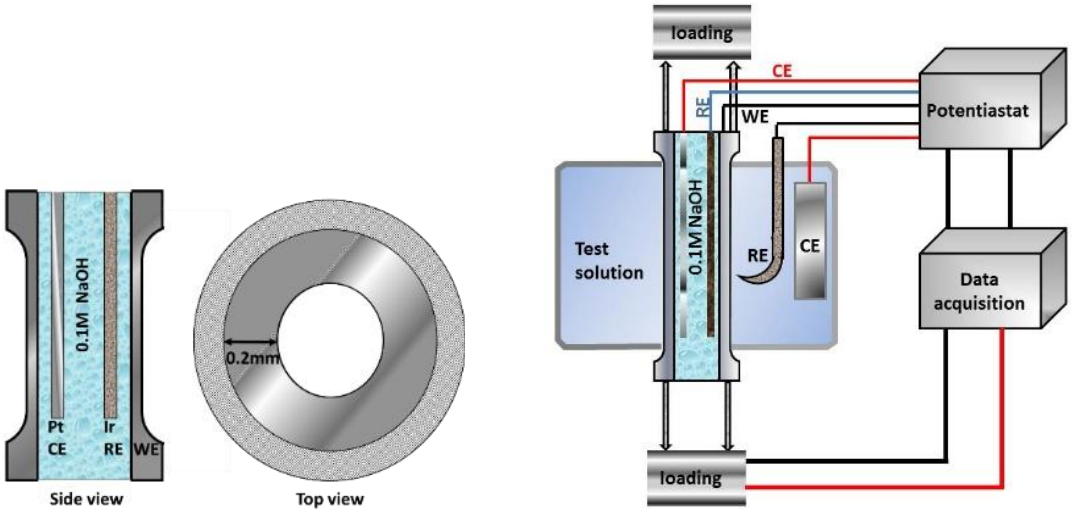

Figure 1. The experimental setup

3. RESULTS AND DISCUSSION

3.1. Background passivation current density in elastic deformation

In order to clarify the effect of the stress on the background current, an experiment was carried out in plastic deformation range as following: loading -stopping -statically loaded- unloading- loading again- stopping (while the stress is bigger than previous stopping) - statically loaded again. Figure 2 presents variation in background current density of the specimen with different loading process in elastic deformation range.

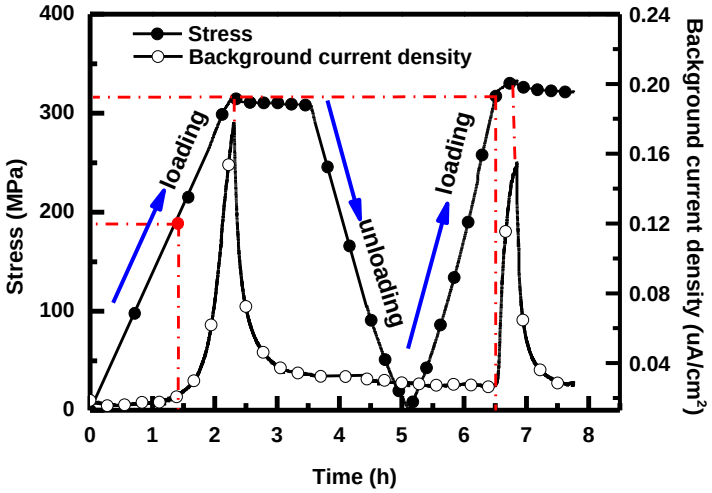

Figure 2. Background current density with different loading process in elastic deformation range Ir as reference electrode, Pt as counter electrode, strain rate is 10^{-7} s^{-1}

At first, the background current density keep steady with increasing stress, after the stress is above 210 MPa, the background current density begin to increase; once the loading stopped, the

background current density began to decrease quickly; the background current density almost have no change in the second loading stage while the stress is lower than previous loading stage. After the stress is bigger than that in previous loading stage, the background current density increase sharply. While the loading stopped, the background current density decrease to previous level again.

At first loading stage, the background current density begin to increase while the stress is above 210MPa. Two factors can affect the background current density, one is the Ni coating damaged, the other one is lattice expansion. When a Ni-coated steel is subjected to stress above the yield strength (YS) of Ni (<250 MPa), the Ni coating film is plastically deformed, thus, the background current density become unstable [12]. Furthermore, according to Kim [12], the apparent diffusivity (D_{app}) value decreased slightly with increasing applied elastic load, and the apparent solubility (C_{app}) value increased, which indicated that the hydrogen amount in lattice and reversible traps increases with increasing applied load in elastic range. The H trap concentration have no relation with the elastic deformation, the elastic loading induced lattice expansion, indicating that the steel can accommodate more H atoms interstitially under tensile stress. So, the increasing of background current density is due to the damage of Ni coating. This also can be proved by the second loading process. In the second loading process, background current density had no change until the stress is bigger than previous loading process. After the stress is bigger than previous one, the thin Ni coating was damaged, more and more fracture generated and more and more base metal exposed to the solution. Which indicate that, the increasing of background current density only related to the damage of Ni coating.

While the stress was stopped, the fresh metal exposed to solution was passivated again, and the background current density was rapidly decrease. This indicate that, if the stain rate lower enough, the change of background current density can be ignored.

3.2. Background passivation current density during SSRT

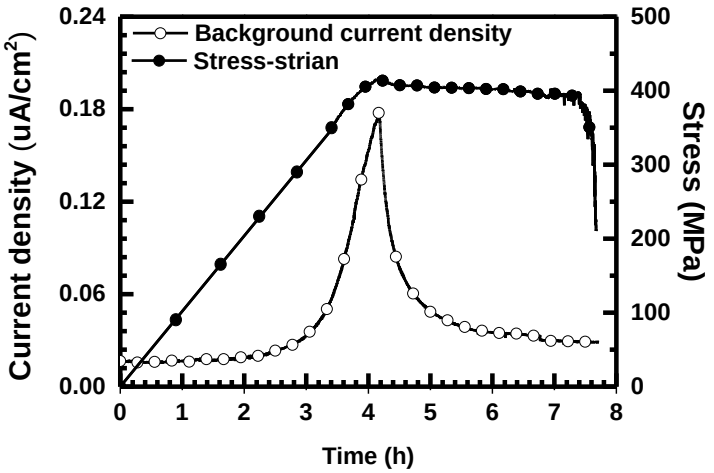

Figure 3. Background current density of the specimen during SSRT Ir as reference electrode, Pt as counter electrode, strain rate is 10^{-7} s^{-1}

Fgiure 3 shows the background passivation current density during SSRT. The background current density increase in elastic deformation range, and then decrease sharply in plastic deformation

range. In elastic range, after the stress above YS of Ni (<250 MPa), the coating film of Ni is plastically deformed, the background current density become unstable. After reaching plastic range of specimen, lots of dislocations are generated and captured and trap H atoms, a large amount of hydrogen was trapped by dislocations, hence the passivation current density decreased sharply.

3.3. Hydrogen permeation current density during SSRT

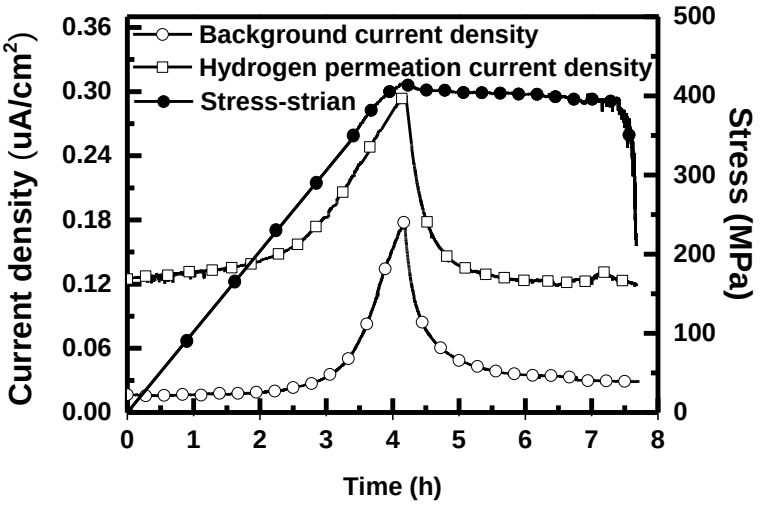

Figure 4. The background current density and apparent hydrogen permeation current density (including background current density) during the SSRT process Ir as reference electrode, Pt as counter electrode, strain rate is 10^{-7} s^{-1}, test solution is 3.5%NaCl

Figure 4 shows the background current density and apparent hydrogen permeation current density (including background current density) during the whole SSRT. From figure 4, the current density increase with elastic deformation, and suddenly decrease after plastic occurred. Subtracting background current density from hydrogen permeation current density, figure 5 was obtained.

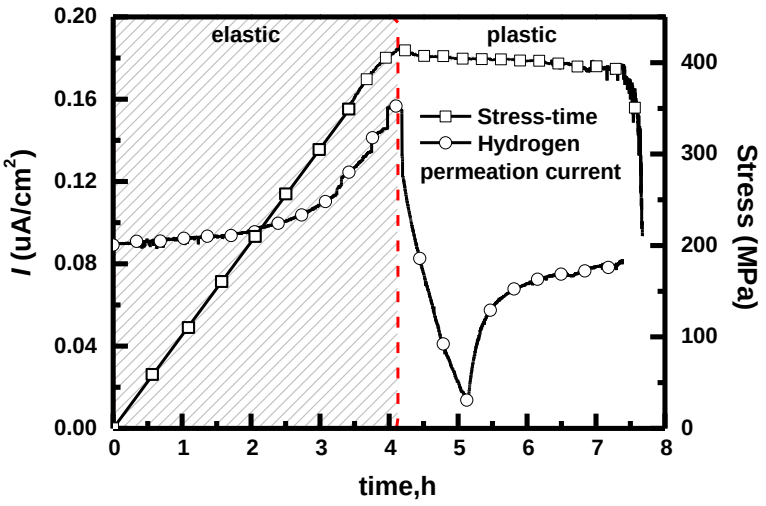

Figure 5. The hydrogen permeation behavior during SSRT process

Figure 5 shows the hydrogen permeation behavior in the whole SSRT. From figure 4 and figure 5, the background current density and hydrogen permeation current density began to increase at about 2.5 hours after experiment. But hydrogen permeation current density increased quickly than background current density. This indicate that, in elastic deformation range, the lattice expansion makes H atom can permeate into and through steel after the reversible dislocation traps saturate.

The hydrogen permeation current density increases with the elastic deformation increase in elastic range. In elastic deformation, reversible dislocations and lattice expansion occurred. After the reversible dislocation traps saturate, only lattice expansion have influence on hydrogen permeation. At a hydrogen permeation steady state, the permeation current density can be written as [4]

$$P_t = D_L C_0 / L \quad (1)$$

Where P_t is the steady permeation current, D_L is lattice diffusivity, C_0 represents the surface hydrogen concentration, L represents the thickness of specimen. According to literatures [4], the diffusivity decreased with the deformation increased, C_0 increase or specimen thickness decrease induced P_t increase. However, the deformation in the test was not more than 0.2%, the contribution of thickness decrease can be neglected. Therefore, increase of C_0 is the main reason. According to literature [4], the surface hydrogen concentration have relationship with corrosion rate, surface coverage of H. The active sites generated on the metal surface, such as lattice expansion or oxide film cracking. And these active sites act to enhance both the reduction of hydrogen ions and also the entry of hydrogen into the lattice. The enhanced entry of hydrogen results in an increase of surface H concentration and thus the permeation current.

3.3. Plastic deformation effect on hydrogen permeation

Lots of dislocations are generated during plastic deformation. And lots of hydrogen atoms gathered in these dislocations and cannot diffuse through the steel. The measured hydrogen permeation current density quickly decreased. The H atoms binding energy in body-centered cubic alloys is much higher than face-centered cubic [9]. In other words, the trapping of H atoms was enhanced in ferritic steels, while dislocations generated in plastic range, the apparent diffusivity of H decreased.

Finally, the trap will saturate by H atoms. After the dislocations saturate, hydrogen atoms diffuse and through the steel under concentration gradient. The permeation current also increases with plastic deformation increase []. The measured hydrogen current reaches steady while dislocations trapping and dislocations moving reached balance. The following assumptions may be used for modelling:

(i) It is assumed that dislocations were created at the surfaces and sweep through grain boundary, then travelled through specimen.

(ii) Dislocations can obtain hydrogen quickly and reached a balance with lattice concentration.

(iii) The lattice have no change in the dislocations movement.

The hydrogen permeation current can be written as

$$P = DC_1 / L - DC_0 / L = D(C_1 - C_0) / L = DC / L \quad (2)$$

D represents lattice diffusion constant, C_1 and C_0 represent lattice hydrogen concentration after and before applying stress. In this paper, a lattice diffusion constant for pure iron of 8.25×10^{-5} cm^2 s^{-1} was taken. Assuming the increasing of hydrogen permeation is due to H escaping from dislocations, the concentration of H captured by dislocations can calculated by subtracting C_0 from C_1 [15]. Figure 6 shows the calculated and measured values.

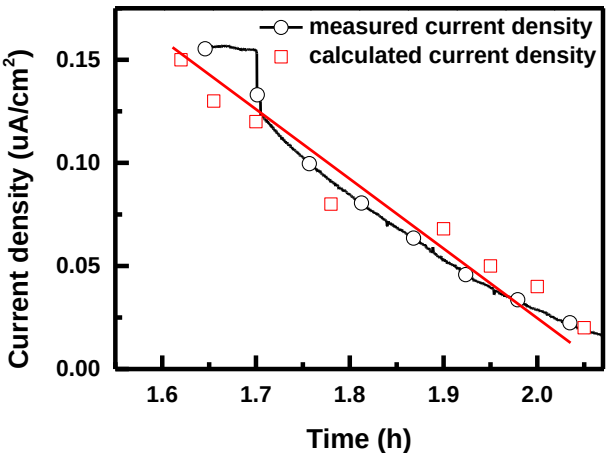

Figure 6. The relationship between measured hydrogen permeation and calculated dislocations trapping current

Considering the experimental error, the slope of calculated values fits the slope of the earlier measured current change well. Therefore, at beginning the hydrogen permeation current decrease was due to hydrogen trapping by dislocations.

4. CONCLUSIONS

Hydrogen permeation behavior during SSRT was studied. Following conclusion are obtained.

1) Background current density increase with deformation increase in elastic rang, the main reason is the Ni coating damaged.

2) Lattice expansion is the reason of hydrogen permeation current density increases in elastic deformation.

3) The Hydrogen permeation current density decreased sharply at beginning due to dislocations (and their trapping of hydrogen) increase sharply. The hydrogen permeation current density reach a steady level after the hydrogen traps are filled and the dislocations can moved by applied stress.

ACKNOWLEDGEMENT
This work was financially supported by the Natural Science Foundation of Jiangsu Province, China (No. BK20141292)

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