Visualization of hydrogen diffusion in steels by high sensitivity hydrogen microprint technique

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Abstract

Hydrogen diffusion in steels was examined by both a high sensitivity hydrogen microprint technique (HMT) and an electrochemical hydrogen permeation method. The main diffusion path in an extremely low carbon steel was lattice within grains; grain boundaries were not accelerated diffusion paths. In the case of a hypo-eutectoid steel, hydrogen diffused through proeutectoid ferrite and ferrite in pearlite under steady-state of hydrogen diffusion. The diffusion paths, however, were carbide/ferrite interfaces when hydrogen charging was interrupted before achievement of the steady state. This is probably ascribable to the reversible trapping effect of the interface. The detection efficiency of the high sensitivity HMT was 75% for the low carbon steel and 40% for the hypo-eutectoid steel.

Keywords: Hydrogen diffusion; Hydrogen visualization; Steels

1. Introduction

Hydrogen embrittlement of steel is caused by hydrogen atoms intruding from the environment [1]. Although the mechanism of crack nucleation and its propagation is a controversial question, many researchers believe that hydrogen atoms diffuse in steel and accumulate at a stress concentration region before the crack nucleation. Thus, it is important to determine the hydrogen diffusion path in steels. However, hydrogen diffusion in steels is very complicated because of the complex microstructure and hydrogen trapping effect of grain boundary, dislocation, precipitation and vacancy [2].

Hydrogen diffusion in steels at room temperature has been studied mainly by an electrochemical hydrogen permeation method. Chan and his co-workers [3] studied the effect of carbon content on the hydrogen diffusion coefficient in steel. Johnson et al. [4] investigated the effect of microstructure on the hydrogen diffusion behavior in steels using samples with a structure of martensite, pearlite, or spheroidized carbide. They analyzed the hydrogen permeation curves in detail focusing on microstructural parameters such as an interfacial carbide area, and discussed the trapping effect of carbide and dislocation. However, the permeation curve obtained by the hydrogen permeation method provides little information on hydrogen diffusion path.

Luu and Wu [5] compensated for this defect of the permeation method by using one of the hydrogen visualization methods, the hydrogen microprint technique (HMT), which was developed by Ovejero-Garcia [6,7]. This technique utilizes a reduction effect of hydrogen atoms released from the specimen surface, and hydrogen exit sites are visualized as silver particles reduced by hydrogen. In this study, Luu and Wu developed the study of Johnson et al. [4], and observed a hydrogen diffusion path in steels with various microstructures using HMT. In a recent study, however, the hydrogen detection efficiency of HMT, which is defined as the ratio of the amount of silver particles to the amount of hydrogen released, has been shown to be extremely low (about 1%) if applied to steel in a conventional manner [8]. This may indicate that the visualization result of Luu and Wu did not reflect the primary distribution of hydrogen in the steels.

Thus, in the present study a high sensitivity HMT recently developed by improving the conventional technique [8] was employed for more precise observation of the hydrogen diffusion path in steel samples. Detection efficiency was also examined by determining the amount...
of hydrogen released from the specimen surface using the electrochemical hydrogen permeation method. The high sensitivity HMT is briefly introduced and compared with the conventional one in the following chapter.

2. High sensitivity HMT [8]

2.1. Principle of high sensitivity HMT

Fig. 1 shows the principle of the high sensitivity HMT schematically. A nickel-plated sample is coated with a photographic emulsion which contains silver bromide crystals. When hydrogen atoms are released from the specimen surface, they reduce silver ions in the crystals to metallic silver. After the remaining crystals are dissolved in a photographic fixing solution, hydrogen exit sites can be visualized as silver particles.

2.2. Determination of detection efficiency of HMT

Since it is impossible to measure directly the amount of hydrogen released in the HMT test, the electrochemical hydrogen permeation method was used under the same charging conditions as the HMT test. As schematically shown in Fig. 2, the same cathodic cell is used for both HMT and the hydrogen permeation test, and the amount of silver on a HMT test sample is compared with the amount of hydrogen determined by the hydrogen permeation method.

2.3. Spatial resolution

The spatial resolution of the conventional HTM is known to be of the order of 0.1 μm when a photographic emulsion containing fine silver bromide crystals (e.g. 0.11 μm in diameter for Ilford L-4) is used. However, in the previous paper [8] the spatial resolution of the high sensitivity HMT remained unclear because of lack of experimental demonstration. Since there is the possibility of decrease in the resolution by hydrogen diffusion in the nickel layer or at the interface between the specimen surface and the nickel layer, the spatial resolution of the high sensitivity HMT will also be discussed in the present paper.

3. Experimental procedure

3.1. Material

Two kinds of steels were used: one is an extremely low carbon steel in a hot-rolled state and the other is a normalized hypo-eutectoid steel. Their chemical compositions are given in Table 1. SEM images of the alloys are shown in Fig. 4. The microstructure of the extremely low carbon steel is fully ferritic (bcc) (Fig. 4(a)), and that of the hypo-eutectoid steel consists of proeutectoid ferrite (bcc) and pearlite (bcc-Fe + Fe3C) as indicated with ‘F’ and ‘P’ respectively in Fig. 4(b).

3.2. Electrochemical hydrogen permeation test

Plate specimens measuring 27 × 27 × 1 mm3 were cut from the two materials. Both sides of the specimens were polished with 1200 grid paper. Then, one side of each specimen was electroplated with a nickel layer 20 nm thick at a constant current of 10 A/m² for 90 s from a Watt bath containing 0.95 mol/l NiSO₄·6H₂O, 0.19 mol/l NiCl₂·6H₂O, and 0.65 mol/l H₃BO₃ [9]. The specimen was mounted on the hydrogen permeation device in such a manner that the nickel-plated side faced the anodic cell as is shown in Fig. 2(a). The cathodic side was galvanostatically polarized at a constant charging current density of 10 A/m² in a 0.1 mol/l NaOH solution containing 4.2 × 10⁻³ mol/l Na₂S·9H₂O as a hydrogen recombination poison. The anodic side was imparted with a constant potential of 0.196 V vs. SHE (0 V vs.
Ag/AgCl) in a 1.0 mol/l NaOH solution. For both sides of the specimen, the area exposed to the electrolytes was limited by Teflon rings with an inner diameter of 20 mm. Before measurement, the solutions were deoxygenated with N₂ gas for 2 h. Measurements were conducted continuously for 60 min under various charging-time conditions of 5, 20 and 40 min at room temperature.

3.3. High sensitivity HMT test

The plate specimen, 27 × 27 × 1 mm³, was polished with the 1200 grid paper on both sides. One side of the specimen was electropolished to reveal the microstructures shown in Fig. 4. This electropolished surface was successively electroplated with a nickel layer of 20 nm under the same conditions as for the hydrogen permeation test specimen. Then, the electropolished side of the specimen was coated with a gelatin-based nuclear emulsion (Ilford L-4, diluted 2 times), and the specimen was placed in a desiccator to dry the emulsion until a gelatin film was formed. The specimen was mounted on the same cathodic cell as that used for the permeation tests in such a way that the surface without the gelatin film faced the cathodic solution as illustrated in Fig. 2(b). This cathodic cell was placed in a chamber where the temperature and relative humidity were kept at 20 °C and 80%, respectively, and then in this chamber the specimen was charged with hydrogen cathodically under the same charging conditions (current density and charging time) as employed for the permeation tests. After hydrogen-exposure time of 60 min, which corresponded to the measurement time in the permeation test, the specimen was removed from the cell and dipped into formalin for 3 s to harden the gelatin film, with a view to preventing redistribution of silver particles [10], after which the specimen was immersed in a fixing solution of 0.60 mol/l Na₂S₂O₃ aqueous solution for 3 min. After the specimen was rinsed with distilled water and dried, silver particles present on the surface were observed under a scanning electron microscope (SEM) and analyzed with an energy dispersive X-ray spectrometer (EDXS). To prevent corrosion of the specimens, a solution of 1.4 mol/l NaNO₂ was used to dilute the emulsion and produce the fixing solution.

Although the specimens were plated with a 120 nm nickel layer in a similar way as in the previous paper [8], the nickel layer hindered clear observation of the microstructures. Thus the thickness was reduced to 20 nm in the present study for clear observation. For confirmation, the effect of the nickel thickness on the detection efficiency was examined using the eutectoid steel, and it was confirmed that the efficiency remained about 40% when the thickness of nickel layer was 20 nm.

Table 1

|                | C    | Si   | Mn   | P    | S    |
|----------------|------|------|------|------|------|
| Extremely low carbon steel | 0.002 | 0.01 | 0.15 | 0.015| 0.005|
| Hypo-eutectoid steel    | 0.29  | 0.19 | 0.79 | 0.014| 0.005|

Fig. 2. Electrical circuits for (a) the electrochemical hydrogen permeation method and (b) the high sensitivity HMT.
4. Results and discussion

4.1. Electrochemical hydrogen permeation test

Fig. 5 shows the permeation curves for both steels. The curves reached a steady-state after a period of about 10 min from the beginning of charging for both materials. As shown, 5 min charging has not reached steady-state, whereas those of 20 and 40 min have reached it. Permeation rate, diffusion coefficient calculated from the breakthrough time and hydrogen content at the hydrogen charging side are summarized in Table 2. Diffusion coefficient in the hypo-eutectoid steel was about half that in the low carbon steel, and permeation rate in the former was about 94% of that in the latter. These results agree with the general rule that permeation rate and diffusion coefficient decrease with increasing carbon content in steels [3]. These decreases are generally ascribed to the hydrogen trapping effect of carbide/ferrite interfaces.

4.2. High sensitivity HMT results for low carbon steel

Distribution of silver particles on the low carbon steel surface is shown in Fig. 6. Fine white particles observed in the micrographs were identified as silver with EDX. The 5 min charging which dose not reach steady-state results in uniform distribution of fine silver particles both inside the grain and on the grain boundary (Fig. 6(a)). In this figure, somewhat bright image of the grain boundaries is due to an edge effect of SEM observation as shown in Fig. 4(a). Although uniform distribution of silver particles remains for charging conditions of both 20 and 40 min which have reached steady-state (Fig. 6(b) and (c)), the size of these particles constantly enlarges with charging time.

The uniform distribution of silver particles indicates that no preferential hydrogen evolution corresponding to the microstructure occurred for the charging conditions employed in the present study. This finding agrees with that obtained by Luu and Wu [5] using conventional HMT. They studied the diffusion path in 0.05 mass% C steel in a similar way and reported that there was no observation of accelerated diffusion along grain boundaries.

4.3. High sensitivity HMT results for hypo-eutectoid steel

Fig. 7 shows high sensitivity HMT results for the hypo-eutectoid steel. Silver particles localize at ferrite/carbide interfaces on the specimen under the 5 min charging
condition in which the hydrogen permeation current has not reached steady-state (Fig. 7(a)). In this case, few silver particles are observed on proeutectoid ferrite. In contrast, the 20 min charging condition including steady-state shows that many silver particles are present not only at the carbide/ferrite interfaces but also on ferrite in the pearlite microstructure (Fig. 7(b)); moreover, proeutectoid ferrite is now covered with silver particles. Under the 40 min charging condition, ferrite in pearlite and proeutectoid ferrite are completely covered with silver particles (Fig. 7(c)). It should be noted that an SEM image of carbide in pearlite that appears white under the 5 and 20 min conditions (Fig. 7(a) and (b)) looks black in Fig. 7(c) for the 40 min charging condition. This reversal of the contrast of the SEM carbide image is probably due to an increase in secondary electrons from a large accumulation of silver particles on ferrite in pearlite with 40 min charging.

As is shown in Fig. 7, the distribution of silver particles clearly corresponds to microstructure of the specimen.

|                  | Permeation rate (mol/m² s) | Diffusion coefficient (m²/s) | Hydrogen content (mol/m³) |
|------------------|-----------------------------|------------------------------|---------------------------|
| Extremely low carbon steel | $8.2 \times 10^{-7}$         | $1.1 \times 10^{-9}$         | 0.74                      |
| Hypo-eutectoid steel     | $7.7 \times 10^{-7}$         | $5.4 \times 10^{-10}$        | 1.42                      |

Fig. 6. High sensitivity HMT results for extremely low carbon steel: (a) 5 min, (b) 20 min, (c) 40 min charging condition.

Fig. 7. High sensitivity HMT results for hypo-eutectoid steel: (a) 5 min, (b) 20 min, (c) 40 min charging condition.
especially in pearlite. This result proves that the high sensitivity HMT has a spatial resolution on the order of 0.1 μm when a very thin nickel layer of 20 nm is applied.

The result for 5 min charging condition was in accord with the observation by Luu and Wu [5] using conventional HMT. They also demonstrated that the carbide/ferrite interface was a preferential diffusion path for hydrogen, and concluded that main diffusion path was the carbide/ferrite interface in pearlitic steel. However, the present results obtained under the longer charging conditions which include the steady-state did not agree with theirs; the results for 20 and 40 min charging indicate that the hydrogen diffusion path at steady-state diffusion in hypo-eutectoid steel was ferrite in pearlite and proeutectoid ferrite. This idea is supported by experimental results obtained by Hagi [11] through electrochemical hydrogen permeation tests for hypo-eutectoid steels. According to his result, hydrogen permeation rate and diffusion coefficient in hypo-eutectoid steels decrease with increasing carbon content, i.e. the volume fraction of carbide. This tendency indicates that ferrite is a main diffusion path and that the carbide/ferrite interface in pearlite acts as trapping site and delays hydrogen diffusion in steels.

However, the question remains why silver particles were localized at carbide/ferrite interfaces under the 5 min charging condition. The explanation may be as follows. The decay curve of the hydrogen permeation test for the 5 min charging condition (Fig. 5) shows that the permeation current for the hypo-eutectoid steel decreases more slowly than that for the low carbon steel. This suggests that hydrogen atoms were reversibly trapped at the carbide/ferrite interface. As a result, hydrogen atoms perhaps diffused along these interfaces at the unsteady-state.

4.4. Detection efficiency of high sensitivity HMT

In Fig. 8 the amount of silver on the HMT specimen surface is plotted as a function of the amount of hydrogen determined by the permeation method. The manner of the determination of silver was described earlier [8]. In low carbon steel, the amount of silver linearly increases with the amount of hydrogen. However, the hypo-eutectoid steel does not show a linear relation; this efficiency was almost zero for the 5 min charging condition. The detection efficiency was calculated from the relationship by the method of least squares to be about 75% for the low carbon steel and 40% for the hypo-eutectoid steel.

The detection efficiency of 75% for the low carbon steel markedly differs from that for the eutectoid steel being about 40%, and is perhaps affected by the microstructure of the specimen used. The extremely low detection efficiency for the hypo-eutectoid steel under the 5 min charging condition might be a notable example of this microstructure dependence. In this case, as suggested by the HMT test results, hydrogen atoms were locally evolved at the carbide/ferrite interface and these localized hydrogen atoms tended to recombine without the reducing silver ions. This might have resulted in decrease in detection efficiency for the hypo-eutectoid steel under the 5 min charging condition.

5. Summary

Hydrogen diffusion paths in the steels were examined with special attention to diffusion path by high sensitivity HMT. Major findings are summarized below:

1. The main diffusion path in the extremely low carbon steel was lattice. No accelerated diffusion of hydrogen along the grain boundary was observed.
2. In the hypo-eutectoid steel, proeutectoid ferrite and ferrite in pearlite were the main diffusion path. Under the charging condition of an unsteady state, hydrogen diffuses along the carbide/ferrite interface because of the trapping effect of the interface.
3. High sensitivity HMT had a spatial resolution on the order of 0.1 μm.
4. The detection efficiency of the high sensitivity HMT was 75% for the extremely low carbon steel, and 40% for the hypo-eutectoid steel. The detection coefficient may depend on the microstructure of the specimens used.

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