Effect of Oxide Film on the Reduction of Hydrogen Permeation Rate in Stainless Steel

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Characteristics of hydrogen permeation in the stainless steel 304 modified by either facing, ion sputtering, carbon coating or annealing were investigated in order to establish the safe hydrogen-energy-infrastructure using welding. A stationary hydrogen flux from the stainless steel surface was measured by using a system with an orifice. The pressure difference of the specimen was able to maintain constant by controlling the gas flow rate from the orifice in low pressure vessel. The hydrogen permeability was low in two cases of a thin stainless steel with fine facing and that annealed at 1 370 K for 2 hours. In these cases, the specimens’ surfaces were considered to play hydrogen trap role and to prevent from pairing hydrogen atoms. On the other hand, high hydrogen permeability was obtained in the case of Argon plasma cleaning a low-pressure-vessel side surface. These results suggest that oxide film on the specimens’ surface prevent hydrogen desorption.

Key Words: Hydrogen, Permeation, Oxide Film, Stainless Steel, Modification

1. Introduction

In order to establish the infrastructure of handling hydrogen safely, for example, a tank of natural gas, a hydrogen gas chamber, a hydrogen fuel cell and a ultra high vacuum chamber, hydrogen permeation phenomena into various materials have been investigated. These tanks and chambers which need no leak of the gas are assembled by welding.

We have performed hydrogen permeation tests against welded specimens. By using a delay time method for estimating the diffusion coefficient, the hydrogen permeability coefficient obtained for the welded specimens was three times greater than the non-welded control(1).

On the other hand, it is useful for preventing hydrogen embrittlement in the heat affected zone that the surface modification has been used to reduce hydrogen induced failures. Various surface modifications for stainless steels, for example boron nitride-coated, nickel plated and so on(2)–(6), have been reported, but the number of reports about the hydrogen permeability for the surface modification for welded stainless steels was a little. The surface conditions of the welded specimens are considered to influence on the hydrogen permeability.

In this study, the hydrogen permeation technique using an orifice and a quadrupole mass spectrometer (QMS) is utilized to measure the hydrogen gas flux in the stainless steel. This work is devoted to considering the hydrogen permeation through the heat affected zone of the stainless steel with the oxide film or non-one on the surfaces.

2. Experimental Method

2.1 Specimens

The specimens were flat-rolled stainless steel 304. Grain sizes were changed by annealing in argon gas at 1 370 K for 2, 4 and 8 hours. Then, their surfaces were polished, and their thicknesses became to be 0.3 mm. Their surfaces were prepared by either facing, oxidizing, ion sputtering or carbon coating. The procedure for the specimen with non-oxide film was cleaning the surface by argon ion sputtering for 10 minutes according to the result shown in Fig. 1 in order to break the oxide film and was coating with carbon for preventing to form metal-oxide. The metal-oxide layer was broken at about 2 minutes shown as a solid line symbolized by solid circle. A series of surface modification of specimens annealed for 2
Table 1  Surface modification of the specimen

| Specimen No. | Annealed in argon | Surface modification |
|--------------|-------------------|---------------------|
| Control      | Non-annealed      | Oxidizing           |
| 1            | For 1h            | Oxidizing           |
| 2            | For 2h            | Oxidizing           |
| 3            | For 2h            | Oxidizing           |

2.2 Permeation method

Figure 2 shows how to set the specimens to the hydrogen permeation test system. The specimen was fixed between two ICF flanges with two copper gaskets as shown in Fig. 2, and the joint divided by the specimen into the high pressure vessel and the low pressure vessel. Then the vessels were evacuated in order to check the leak at the joint of fixed the specimen, before the mixed gas of 10 vol% H₂ + Ar was introduced into the high pressure vessel.

The scheme of the measurement system with an orifice is shown in Fig. 3. Three vessels, composed of the high pressure, the low pressure and the analysis vessel, can be evacuated all at once. The pressure difference of the specimen was able to be kept constant by controlling gas flow rate from an orifice in the low pressure vessel, although it never reached equilibrium during the measurement using our usual system for a delay time method for estimating a diffusion coefficient \(^{(1)}\).

Thermal cycle for the hydrogen permeation measurement is shown in Fig. 4. After three vessels were evacuated, the specimen was baked at 720 K for 4 hours in order to diminish degassing of H₂O gas from the specimen. Then the mixed gas of 10 vol% H₂ + Ar was introduced into the high pressure vessel after keeping the test temperature 620 K for 1 hour and the hydrogen pressure (Outgass of H₂O is considered to include hydrogen) was measured by QMS in the analysis vessel. The analysis and low pressure vessel was evacuated by a turbo molecular pump attached the analysis vessel while the measurement. The hydrogen permeation tests were performed two times every specimen to confirm the stable partial pressure of hydrogen gas.

3. Estimation of Hydrogen Permeability, K

Volume flow rate through the orifice, \(Q\) is estimated from the Eq. (1), using QMS output value, \(P_{\text{total}}\).

\[
Q = (P_{\text{low}} - P_{\text{total}}) A \sqrt{\frac{k T_{\text{low}}}{2 m}}
\]  (1)

The pressure difference at the orifice is described as \(P_{\text{low}}\): the pressure in the low pressure vessel, minus \(P_{\text{total}}\): the pressure in the analysis vessel. \(m\) is an average of molecular weight of gases in the low pressure vessel. \(k\) is Boltzmann constant. \(A\) is the area of a hole of the orifice.

For hydrogen gas flux, \(J(t)\) was estimated from Eq. (2) using \(Q\) and the area of the specimen, \(S\) and \(P_{\text{H}_2}\)
is the partial pressure of hydrogen in the analysis vessel detected by QMS.

\[ J = Q \frac{P_{H_2}}{P_{total}} \cdot \frac{1}{S} \]

\[ = (P_{low} - P_{total})A \sqrt{\frac{kT_{low}}{2\pi m}} \frac{P_{H_2}}{P_{total}} \cdot \frac{1}{S} \]  

(2)

Permeability, \( K \) of diatomic molecule was calculated from the Eq. (3), since \( H_2 \) gas is assumed to be an ideal gas,

\[ K = \frac{l \cdot J}{\left( \frac{1}{2} P_{H_2\text{high}} - \frac{1}{2} P_{H_2\text{low}} \right)} \]  

(3)

where \( l \) is the thickness of the specimen and \( P_{H_2\text{high}} \) is the partial pressure of hydrogen in the high pressure vessel.

4. Results and Discussion

4.1 Comparison of mother metal with annealed specimen

The results of \( J(t) \) through the specimen annealed for 2 hours and the control at 620 K are shown in Fig. 5. The line of the hydrogen gas flux results has some spikes. It relates to the sensitivity of QMS in the system. Maximum value of \( J(t) \) at the second time is \( 1.1 \times 10^{-6} \) Pa\( \cdot \)m/s, and it is 1.4 times greater than the first time. Absorbed hydrogen gas atoms trapped in the specimen at the first time permeation test was out from it during the second time test, because the baking time at the interval evacuation was short, and because iron dissolves a small amount of hydrogen atoms endothermically. Figure 6 shows metallograph-images of the specimens’ cross-section. The rolling bands vanished and the grain size became large as shown in Fig. 6. The hydrogen gas flux of the annealed specimen is less than the control. This result suggests that the hydrogen pass-routes are decreased, since the grain size growing and hydrogen gas atoms were trapped in the large grain boundaries of the annealed specimen.

In the cases of the specimens annealed for 4 and 8 hours, argon gas was detected by QMS. Therefore total pressure of the non-argon-leak specimen is lower than one of the argon-leak specimens as shown in Fig. 7. It was considered that argon gas atoms pass through the grain bound-

Fig. 5  Hydrogen permeation \( J(t) \) results of annealed for 2 hours specimen and non-annealed one at 620 K

Fig. 6  Metallograph-images of the specimens’ cross-section of (a) control, (b) annealed for 2h, (c) annealed for 4h, (d) annealed for 8h stainless steel specimens

Fig. 7  Total pressure results during permeation tests against the specimens with argon leak. These specimens were annealed ones for 4 h and 8 h
Fig. 8 Hydrogen permeation $J(t)$ results of annealed for 2 hr specimen and carbon coated one at 620 K

aries of the specimens annealed 4 and 8 hours, because the simple straight grain boundaries which pass across the plates can be observed in Fig. 6.

4.2 Influence of oxide film

Figure 8 shows the hydrogen gas flux results during the hydrogen permeation tests. These specimens were annealed at 1 370 K for 2 hours. The greatest values are obtained against the specimens with the low-pressure-side surface cleaned by argon ions sputtering and coated with carbon. The least values are obtained against the specimen with the oxide film surfaces both sides. In the case of the former specimen, the hydrogen gas flux data at the second time test are greater than at the first time test. The reason why the value at second time test was greater than that at first time test is considered to be outgas of hydrogen atoms at the grain boundaries. The oxide film on the high-pressure-side surface is considered to accelerate absorption of hydrogen gases and separation of hydrogen atoms.

In the case of the specimen with the high-pressure-side surface cleaned by argon ion sputtering and coated with carbon, there is no difference between the hydrogen gas flux data at the first time test and the second one as shown in Fig. 8. The values are $1.2 \times 10^{-6}$ Pa·m/s. This result suggests that the oxide film on the low-pressure-side surface prevent hydrogen atoms from pairing and desorbing of hydrogen gases.

The reason of the least value of $8.0 \times 10^{-7}$ Pa·m/s against the specimen with oxide films both side surfaces is considered that high concentration of hydrogen atoms at trap sites in the specimens due to sealing with low-pressure-side oxide film.

4.3 Comparison of permeability

Relationship between permeability and temperature acquired by the system with an orifice is shown in Fig. 9. The difference of permeability shown as a solid square and a solid rhomb between the thicknesses of 1.0 mm and 0.3 mm is due to surfacing, since visual observation of the two specimen made clear the difference of fine surface oxide film and not so fine surface film.

When the specimen’s surface oxide film was broken, as shown by a vacant circle in the figure, the permeability is identified with the specimen, which has not so fine surface. When the specimen’s surface was covered with a fine oxide film by annealing for 2 hours shown as a vacant square is identified with the material which has fine surface. It indicates that fine surface oxide film impede the hydrogen permeation.

If the stainless steel 304 is heated for a long time at the high temperature from 670 K to 1 070 K, the intergranular corrosion tended to occur. Two gradients of the solid lines against controls are almost same one against the iron as shown by a solid line in this figure. These results are considered to be related to intergranular corrosion in the stainless steel specimens.

5. Conclusion

Hydrogen permeation tests for annealed stainless steel with the oxide film or non-one on the surfaces were performed in order to consider the reason why the hydrogen permeation through the heat affected zone of welded specimens increase. The results are as follows.

Low hydrogen permeation coefficients were obtained for the Stainless steel specimens with fine faced surfaces with fine oxide film and specimens annealed for 2 h with course grains and fine oxide film. It is considered that hydrogen traps exist in grain boundaries of each stainless steel specimen. The effect of the traps on the hydrogen permeation was greater than the traps of band structure.

In the cases of the hydrogen permeation tests for the specimens with clean surfaces by sputtering, the results were different from the fine oxide film ones. The oxide
film on the low-pressure-side surface prevents hydrogen atom pairing and desorbing of hydrogen gas. On the other hand, the oxide film on high-pressure-side surface accelerates absorption of hydrogen gas and separation hydrogen atoms. Hydrogen atoms are trapped between oxide film on the low pressure vessel side and the stainless steels metals.

For the annealed specimen, the gradient of the hydrogen permeation coefficient versus $1/T$ was same as that of the iron. It indicated that hydrogen pass routes in the annealed stainless steels became as same routes as iron body-centered lattice material.

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