—Communication—

Promotion of Pitting for Type 304 Stainless Steel by Permeated Hydrogen

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1 INTRODUCTION

Evolution of hydrogen is one of the typical cathodic reaction involved in the localized corrosion process of passivated materials. Although the diffusivity of hydrogen within austenitic stainless steel is very low ($\sim 10^{-12}$ cm²/s¹⁾) because of its f.c.c. structure, it has been shown that the uptake of hydrogen is possible even under open circuit condition in deaerated solutions at 368 K²⁾. Some amount of hydrogen might diffuse to the surface and affect the passive film, as has been suggested for iron and nickel³⁾. In spite of extensive works on hydrogen embrittlement of steels, limited data is available on the change in resistance of passive film against localized corrosion by hydrogen. Hasegawa and Osawa showed that stainless steel that absorbed hydrogen under high temperature and pressure suffered anomalous corrosion, which might be caused by the formation of activated microdefects and unstabilization of passive films^{4,5)}. Armacanqui and Oriani⁶⁾ found that passivated nickel became less resistive to pitting by permeated hydrogen using Devanathan's type of cell⁷⁾. In the present study, this type of pitting tests have been carried out on type 304 stainless steel.

2 EXPERIMENTAL

Commercially available type 304 stainless steel foil (50 μ m thick) was cut into disk, electropolished in CrO₃-H₃PO₄-H₂O, and rinsed. One side of the specimen was sealed leaving about 1 cm² area, which was submitted to pitting test. Both side of specimen was again electropolished briefly and rinsed ultrasonically. The specimen was assembled into a Devanathan's type of cell which contained 260 cm³ of deaerated 0.1 M Na₂SO₄ in a cathodic compartment and 0.1 M Na₂SO₄ + 0.5 M NaCl in an anodic one.

Hydrogen was charged galvanostatically (-1 mA/cm²) from a cathodic compartment for 24 hours, while open circuit potential of the other side of the specimen was monitored. Then, an anodic polarization curve was measured at 100 mV/min in the anodic compartment. Impedance measurement was also carried out for anodic side.

In the separate experiments, the anodic side of a specimen was polarized to the passive region (250 mV vs. SHE at 343 K) in chloride free solution, while hydrogen was charged from cathodic side for 24 hours. Then, NaCl was added to anolyte so that the concentration of chloride became 0.5 M and induction period for pit initiation was measured.

All experiments were carried out at 343 K. Potentials measured against Ag/AgCl/KCl(0.5 M) reference electrode were converted into SHE scale at 343 K.

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3 RESULTS AND DISCUSSION

Fig. 1 shows variation of corrosion potential of anodic side with or without hydrogen permeation. With progress of permeation of hydrogen, the corrosion potential became less noble and reached around -400 mV, which corresponded to redox potential for hydrogen at the pH of this solution ($5.5 - 6.0$). The impedance measurement showed that the apparent film resistance reduced significantly (from 2×10^6 to $4 \times 10^3 \Omega \text{cm}^2$) while the apparent capacitance increased (from 150 to $250 \mu\text{F cm}^{-2}$), suggesting that the film suffered changes in thickness and composition.

Fig. 2 shows the polarization curves of anodic side after 24 hours charging of hydrogen. In chloride free solutions, the difference between line 1 and 2 is attributed to oxidation of permeated hydrogen and accelerated transpassive dissolution⁸⁾. Pitting potentials observed in chloride containing solutions had significant difference between charged and uncharged specimen. Appar-

ently, hydrogen seems to enhance the pitting susceptibility of stainless steel.

Since pitting is usually characterized by pitting potential and induction period, the effect of hydrogen on the induction period was examined. Anodic side of specimen was polarized at 250 mV for 24 hours during charging of hydrogen from cathodic side. The induction period for pit initiation after addition of NaCl typically distributed 10 through 20 minutes. Since pitting period is strongly depends on passivation time, the induction period for an uncharged specimen was measured as a function of it at 250 mV. When NaCl was added to the solution after passivation at 250 mV for 24 hours, the induction period ranged from 78 to 296 minutes, while it did not exceed 30 minutes when NaCl was added just after the specimen was polarized at 250 mV. The induction period for pitting has been recognized to become

Fig. 1 Variation of corrosion potential of type 304 stainless steel with permeation of hydrogen at 343 K

Solution: $0.1 \text{ M Na}_2\text{SO}_4$ for 1 and 2
 $0.1 \text{ M Na}_2\text{SO}_4 + 0.5 \text{ M NaCl}$ for 3 and 4

Fig. 2 Effect of permeated hydrogen on the anodic polarization behavior of type 304 stainless steel at 343 K

Solution: $0.1 \text{ M Na}_2\text{SO}_4$ for 1 and 2
 $0.1 \text{ M Na}_2\text{SO}_4 + 0.5 \text{ M NaCl}$ for 3 and 4

Scan rate: 100 mV/min

longer with ageing of passive film⁹). The permeated hydrogen seemed to reduce this ageing effect.

The induction period for pitting is known to depend on both film thickness and composition⁹). It may be possible that the permeated hydrogen reduces passive film, which results in thinning of it. The permeated hydrogen may also change the composition of films as has been pointed out by Pyun and Oriani³). Furthermore, the oxidation of permeated hydrogen at the film/solution interface might enhance the local concentration of hydrogen ion. Transition of austenitic phase to martensitic one at anodic side would not be significant, since it is limited to charging surface layer of 8 μm depth even under severe charging condition¹⁰). Although the precise role of hydrogen is not clear in the present stage, elucidation of it would lead to better understanding of general pitting mechanism and characterization of passive films.

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