A mechanistic study on the hydrogen trapping property and the subsequent electrochemical corrosion behavior of quenched and tempered steel

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ABSTRACT

The hydrogen-facilitated anodic dissolution of steel is an interesting experimental phenomenon, but the persistent gaps in this knowledge area are great. The changes in the Tafel slopes and the reaction rates of steel that has been cathodically charged with hydrogen are interpreted mainly in the context of hydrogen trapping and de-trapping behaviors of steel using a variety of electrochemical methods. This study reveals that the increase in the anodic current density and the decrease in the polarization resistance are attributed primarily to the hydrogen-induced lattice expansion. Based on the Tafel-slope change, the oxidation of hydrogen cation partly contributed to the increase in the total anodic current density together with the dominant anodic reaction of the steel dissolution. The electrochemical permeation measurements showed much slower effusion kinetics of the hydrogen that has been trapped at the ε-carbide particles, and the trapping and de-trapping behavior at the fine particles are one of the controlling factors of the hydrogen-enhanced anodic dissolution of steel. From an engineering aspect, it is believed that the current study will provide an important insight into future perspectives on stress corrosion cracking failure occurring in various high-strength steels.

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Introduction

The Hydrogen-activated anodic dissolution of metallic materials is one of the interesting experimental phenomena that have been recently accepted in the electrochemical field. Numerous researchers have demonstrated that the kinetics of steel dissolution are apparently enhanced in steels that have been charged cathodically with hydrogen. Although they have presented several mechanisms for the phenomenon [1—4], the exact nature has not been completely clarified; in particular, it is still unclear whether the enhanced anodic currents measured electrochemically are purely attributed to the steel dissolution (Fe → Fe^{2+} + 2e$^-$). A previous study [5] posed a yet unproven possibility that hydrogen that has been desorbed from steel may contribute to the increase in anodic current by the oxidation reaction (H → H$^+$ + e$^-$), like the case of the

detection part of the hydrogen permeation process [6]. It has also been proposed that there is the possibility of enhanced anodic dissolution by the reduction of iron oxide film during the desorption of hydrogen from the pre-charged steel [3]. It is in the previously explained context that the surface-cleaning effect of absorbed hydrogen has been used in academic circles. Li et al. [1] attributed the phenomenon to the alteration of the chemical potential and exchange current density of steel; however, this has not been experimentally demonstrated. Another mechanism is based on the weakening of the Fe—Fe bonding strength that is caused by the presence of hydrogen in the steel lattice at the sub-surface, leading to a decrease in the activation energy for steel dissolution. This hydrogen-driven decohesion phenomenon has been supported by the first principles modeling conducted by Thomas et al. [5]. However, numerous questions still remained unanswered in this topic. From an engineering perspective, the clarification of underlying mechanism for hydrogen-facilitated dissolution has a significant insight into stress corrosion cracking (SCC) failure of metallic materials exposed to near-neutral pH environments [7,8]. Since it is considered that the cracking susceptibility depends greatly on a synergistic effect of hydrogen and anodic dissolution, the aforementioned uncertainties in the hydrogen-assisted corrosion behaviors of high-strength steels should be urgently clarified. To accomplish these works, the relationship between the presence of hydrogen in the steel and resultant corrosion behaviors is established in this study. For this, a variety of electrochemical evaluations were conducted for the steel samples of uncharged, pre-charged, and aged following the pre-charging. In addition, to gain further insights into the iron carbide particles with slow effusing kinetics of hydrogen, the electrochemical permeation technique was used.

Experimental

Specimen preparation and microstructure observation

The test material used in this study was ultra-strong steel with a tensile strength of approximately 2 GPa. The chemical composition of the steel is briefly summarized in Table 1. The steel sample produced by the steel manufacturer (Pohang Iron and Steel Company) was reheated to 1200 °C for 2 h, and then it was hot- and cold-rolled into a 2 mm thickness. Then, the sample was austenitized by heating at 930 °C for 7 min and subsequently quenched in water. The quenched steel was tempered additionally at 200 °C for 30 min. The microstructure was observed using the field-emission scanning electron microscope (FE-SEM). The fine precipitates contained in the microstructure were observed and analyzed using the transmission electron microscopy (TEM). Additionally, the

fractions of carbides in the microstructure were determined using the electron backscatter diffraction (EBSD) analysis.

Cathodic hydrogen charging and subsequent aging process

Hydrogen was introduced cathodically into the steel samples by applying a constant cathodic current density of 5 mA/cm^2 for 1 h in a 0.5 M NaH$_2$PO$_4$ + 0.1 M H$_3$PO$_4$ + 0.3% NH$_4$SCN solution. To evaluate the effect of the desorption of the hydrogen from the pre-charged sample, the charged sample was subsequently aged at room temperature for 48 h.

Diffusible hydrogen measurement

After the pre-charging and/or the aging, the diffusible hydrogen contents that were introduced into the samples were measured using the glycerin method in reference to JIS Z3113 [9]. Fig. 1 exhibits a schematic diagram of the glycerin method [10]. The measured volume of the hydrogen that was desorbed from the samples was converted into the unit of ppm using the following Eq. (1) [11].

$$V(ml) = \frac{(h_{1,G} - h_G)V_1 273.15}{8.2(273.15 + T_1(°C))} \tag{1}$$

where V_1 is the amount of hydrogen that was desorbed from the steel specimen, 8.2 is the height of the glycerin column at the standard temperature and pressure, $h_{1,G}$ is the height of the glycerin column at 0 °C and the atmospheric pressure, and h_G is the height of the glycerin column at T_1 and the atmospheric pressure where T_1 is the measured temperature.

Electrochemical impedance spectroscopy and hydrogen permeation measurements

Electrochemical hydrogen charging and the electrochemical impedance measurements were conducted simultaneously using the Devanathan-Starchurski double cell, as depicted in Fig. 2. Contrary to the conventional permeation technique that is illustrated in the ISO 17081 standard method [6], the electrochemical impedance was measured in the hydrogen detection side. During the electrochemical impedance spectroscopy (EIS) measurements that were performed in deaerated 0.1 M NaOH, the cathodic current density of 15 mA/cm^2 was constantly applied to the test sample in hydrogen charging side composed of 1 M NaH$_2$PO$_4$ + 0.1 M H$_3$PO$_4$ + 0.3% NH$_4$SCN. The EIS tests were conducted at the open circuit potential (OCP) with the application of a sinusoidal voltage of a 10 mV amplitude over the frequency range from 10000 to 0.01 Hz.

Besides, to analyze the effusion kinetics of the hydrogen that was introduced into the steel sample, the electrochemical permeation test involving the stepwise sequence of 1st permeation under no applied cathodic charging — desorption — 2nd permeation under an applied cathodic charging was conducted. The 1st permeation was conducted in a 3.5% NaCl solution+0.3% NH$_4$SCN. An applied potential in hydrogen detection side was 270 mV$_{SCE}$. The thin palladium (Pd) film, with 100 nm thickness, was electrochemically deposited to the steel membrane in detection side. For the electroplating, a galvanostatic current density of 1 mA/cm^2 was cathodically

Table 1 — Chemical composition of the test sample.						
Chemical composition (wt.%)						
C	Mn	Cr	Mo	Cu	Ni	Fe
0.3—0.4	1.0—1.5	<0.2	<0.2	<0.1	<0.1	Bal.