Short Communication

Metallurgical evidence of stress induced hydrogen diffusion and corresponding crack nucleation behaviors of high-strength ferritic steel used in sour environment

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Owing to the difficulty in obtaining experimental evidence of stress-facilitated hydrogen-diffusion/trapping behavior, previous studies focused on numerical analyses of electrochemical permeation measurements. To address the weak points of the theoretical approaches and provide strong supporting evidence, the nascent fracture surface of an initial crack formed only under an applied stress was examined. This paper presents two metallurgical findings of clusters comprised of 2nd phase particles and traces of grain/lath boundaries observed in the crack nucleation site of high-strength ferritic steel under an applied tensile stress in elastic range.

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\section*{1. Introduction}

The concept of stress-induced H-diffusion in metallic materials has been widely explored in a number of studies [1–6]. This concept is based on the fact that the distribution of H depends on the formation of tri-axial stress field within the materials, and H can accumulate at some localized regions. Most studies [1–5], however, have been conducted on a theoretical basis due mainly to the difficulty in presenting experimental evidence related to the local accumulation of H in materials under stress conditions. A number of numerical modeling approaches taking into account the effects of stress/strain on H-accumulation in prospective rupture sites have been presented [5], and they were used for the rupture-prediction analyses of metallic materials subjected to any type of H-embrittlement (HE) in service. A considerable number of metallurgists have focused on the mechanical degradation phenomena of metallic materials charged with H by applying a cathodic current in an aqueous media [7–11], and the HE index has been determined simply by the loss of elongation. In addition, previous studies have shown the final fracture surfaces with a quasi-cleavage (QC) pattern obtained after tensile tests. The H-distribution in metallic materials can be presented visually using the hydrogen microprint technique (HMT) with the interaction between AgBr particles and H. A number of studies [12–15], including work by Wang et al. [15] showed preferential H-trapping at various phase...
boundaries in steel using the HMT. This technique, however, cannot guarantee whether the trapping contributes to actual cracking failure or not. Experimental studies using an electrochemical permeation technique (EPT) combined with tensile testing apparatus have also been conducted to understand the H-diffusion behaviors in various metal samples, where the stress field was set up [16–21]. It has been generally accepted that the application of tensile stress in the plastic range to the ferritic steel leads to slower diffusion kinetics due to predominant H-trapping at the dislocation [17,18], while no significant change in H-diffusivity and a slight increase in permeation flux can be observed under the stress conditions in the elastic regime [18,21]. Although this approach provided significant insight into the relationship between the applied stress and hydrogen diffusion behavior of steel, H-accumulation at localized areas with a high stress field has not been demonstrated. A numerical diffusion study based on the permeation experimental data showed that irreversible trapping was predominant at the microstructural-discontinuity in the steel under local-plasticity, resulting in slower diffusion. In addition, a higher irreversible trap density and faster trapping rate from interstitial lattice site to irreversible traps were determined using the numerical finite difference method (FDM) [21]. Although the validity of the numerical study was supported partly by a follow-up paper [22], which described the comparison between two ferritic steels with different levels of 2nd phase particles, there is no direct experimental evidence of H-accumulation at 2nd phase particles under an applied stress. In this study, the crack nucleation process induced by H-diffusion and trapping at microstructural-discontinuity under stress conditions was clarified further by presenting the nascent fracture surface of an initial crack site of high-strength ferritic steel subjected simultaneously to H-charging and tensile loading in the elastic regime.

2. Experimental

The steel used in this study was ferritic carbon steel with 0.2 wt.% of C, which is normally used as pressure vessel steel (ASTM A516-70) in the petrochemical industries. The tested steels were normalized: heating at 910 °C for 4.7 min/cm and cooling to ambient temperature at a rate of 4.5 °C/s using a mixture of oil and water. The final microstructure of the tested specimens was composed of ferrite/scattered pearlite with a high resistance to HIC [23]. To exclude the effect of microstructure on H-trapping or H-assisted cracking behaviors, the tested samples were taken from the center part of the same steel slab.

Electrochemical permeation data reported previously [21] was first discussed in the view point of its inherent weakness. Detailed information of the experimental method and results can be found elsewhere [21].

A HIC test was initially performed in NACE TM0284 solution A [24] for 72 h, and the steel specimen was confirmed to be free of surface blisters. In addition, to apply the tensile stress to the specimen during the HIC test, a constant load to 95% vs. YS of the specimen was applied using a four-point bent beam tester in reference to ASTM G39 [25].

One of the key technical issues in this study was to obtain a nascent fracture surface of an initial crack formed during the HIC test conducted under stress conditions. For this purpose, an efficient method involving a series of mechanical process followed by field emission-scanning electron microscopy (FE-SEM) observation was used, and the detailed procedure is presented schematically in the results section.

3. Results and discussion

Fig. 1(a) shows hydrogen permeation current density under cyclic operation (i.e., 1st cathodic charging-desorption-2nd cathodic charging-desorption-3rd cathodic charging) [21]. In contrast to the case of the 1st permeation, the rising transients of 2nd and 3rd permeation exhibited faster diffusion kinetics of H because the transients were governed only by interstitially diffused and/or reversibly trapped H because of an absence of irreversible traps [21,26]. As reported previously [20,21] and presented in Fig. 1(b), the application of tensile stress to the specimen immediately before the 2nd permeation leads to either a slight increase in $j_{2t}$ under an elastic stress regime or a significant increase in $t_{lag}$ under local/generalized plastic stress regime. This suggests that the application of a high level of tensile stress shows slower diffusion kinetics of H despite the 2nd permeation. Frappart et al. [19] and Kim et al. [21,22] indicated that a micro-plastic area can be formed under tensile stress even within the elastic limit, and it provides additional H-trap sites of expanded interfacial areas around the 2nd phase particles. This stress-induced H-trapping behavior was also supported by presenting a higher $k_{irr}$ value (i.e., an index representing

![Image](image_url)
Fig. 2 – Two different sample preparation procedures for the observation of fracture surfaces of HIBC, and identification of crack nucleation sites from the nascent fracture surface using FE-SEM.

Fig. 3 – Surface morphology observation of the crack nucleation sites appearing as a flat area in (a) low magnification image, (b) area showing 2nd phase particle cluster, (c) area showing traces of grain/lath boundary, and (d) magnified view of the boxed area in (c).
the transition probability for H-transport from the lattice site to irreversible traps) with increasing stress level [21]. On the other hand, they are based mostly on electrochemical analysis with the theoretical diffusion model proposed by McNabb and Foster [27], but direct metallurgical evidences associated with the local accumulation of H in the specimen under stress conditions was not presented clearly. To compensate for this weakness, the author paid particular attention to observations of the nascent fracture surfaces of hydrogen-induced blister cracks (HIBC) occurring only under tensile stress condition.

Fig. 4 presents surface observations after the HIC test under two load levels (0% and 95% vs. YS of specimen), indicating that surface blisters occur only under 95% vs. YS. Because the appearance of surface blisters indicates that cracks were formed below the blister [21], the applied tensile stress contributed directly to the formation of the initial crack (HIBC) in the steel charged with H. Considering that crack formation is closely associated with the activities of H infused readily in the steel under H2S containing environment, one of the key issues in the clarification of stress-induced H-accumulation/trapping is to obtain a nascent fracture surface of HIBC occurring under stress conditions. In general, the crack initiation/propagation behaviors can be analyzed by observing the cross-sectional area, which was polished until the crack appeared, as described in the left side of Fig. 2. On the other hand, as also reported previously [28], this conventional approach cannot provide a nascent fracture surface due to contamination/corrosion in the crack during the mechanical polishing. A more efficient procedure involving a series of mechanical processes for obtaining a nascent fracture surface is provided on the right side of Fig. 2.

With the help of the method described above, the nascent fracture surface of HIBC occurring under stress conditions was clearly observed, which is given at the bottom right in Fig. 2. Such low magnification images revealed flat areas, which were suspected to be a crack nucleation site. An examination of the flat area with a higher magnification (Fig. 3(a) and (b)) provides two significant insights regarding the metallurgical aspects: one is the presence of clusters consisting of a number of 2nd phase particles at the area (shown in Fig. 3(a)). It can be generally accepted that the clusters with a coarse volume size and sharp edges act as a stress concentration under an applied stress. The other aspect is the appearance of grain/lath boundaries in the area (shown in Fig. 3(b)). Such inter-granular/lath fracture of HIBC is generally believed to have originated from the weakening bonding force among the boundaries by the preferential diffusion of H into the boundaries. For a clearer observation, a higher magnification view of the local embrittled areas showing the quasi-cleavage (QC) and inter-granular/lath patterns is given in Fig. 3(c). Considering that the two sets of metallurgical evidence described above were obtained only under the combined action of H-charging and tensile loading, it is reasonable to state that the preferential H-diffusion/trapping at the grain/lath boundaries around the clusters, where the applied stress is highly concentrated, results in inter-granular/lath fracture of HIBC known as initial crack occurring in a sour environment. This mechanistic concept is represented schematically in Fig. 4. Since the cracks detected here were only HIBC and there was no crack which propagates perpendicular to the applied stress, stress relaxation effect during the test of four-point bent beam can be disregarded.

This letter provides significant insight into the mechanistic studies on hydrogen embrittlement of high-strength ferritic steel by providing strong supporting evidence of stress-facilitated H-diffusion behavior of steel in acidic sour environments. The author believes that this letter addresses
the weak points of previous studies [21,22] on numerical analyses of electrochemical permeation measurements.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Conflicts of interest

The author declares no conflicts of interest.

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