

In-situ Observation of Hydrogen-Induced Cracking Initiation Site in Line Pipe Steels

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ABSTRACT

Hydrogen-induced cracking (HIC) is a hydrogen embrittlement phenomenon that occurs in a line pipe exposed to the sour environment. Generally, the initiation site of HIC is estimated by observing the fracture surface after the test. It is reported that typical initiation sites of HIC are non-metallic inclusions, such as elongated MnS, in the center segregation region. However, there is no in-situ observation technique that can establish a direct link between the initiation site and inclusion. In this study, an in-situ HIC measurement technique was developed to observe HIC initiation behavior and identify the initiation site of HIC. This technique is based on the combination of an automatic ultrasonic wave inspection (UT) system and energy dispersive X-ray spectroscopy (EDS). By overlaying the C-scan movie obtained using the UT system on the EDS map of the HIC fracture surface, as in projection mapping, the initiation site of HIC was related to the non-metallic inclusion directly. Additionally, the hydrogen concentration at the HIC initiation site was calculated using finite element analysis, whereas the critical hydrogen concentration (C_{th}) was obtained as the hydrogen concentration at the time of HIC initiation.

Key words: Sour environment, Hydrogen-induced cracking, Inclusion, Hydrogen, Line pipe

INTRODUCTION

In the oil and gas industry, oil country tubular goods or line pipes are exposed to wet H₂S environments (sour environments) in some cases. The presence of H₂S in the sour environment enhances hydrogen entry into the steel due to the catalytic action of H₂S. The absorbed hydrogen enhanced by H₂S affects hydrogen embrittlement. Hydrogen-induced cracking (HIC) is a hydrogen embrittlement phenomenon observed in sour conditions.

To evaluate HIC susceptibility, NACE TM0284 was established.¹ With the establishment of the test method, it has become clear that HIC susceptibility is affected by inclusions, precipitates, microstructure, and hardness.²⁻⁶ Elongated non-metallic inclusions (especially MnS) and insoluble coarse particles (Nb (C, N), TiN) induce the initiation of HIC. As HIC susceptibility increases with the hardness (local maximum hardness) of the steel, a banded microstructure, such as ferrite-pearlite dual microstructure, and center segregated zone also decrease the HIC resistance. Therefore, almost all researchers and manufacturers agree that there are three important factors to achieve resistance to HIC: clean steel, uniform microstructure, and low hardness.

It is recognized that HIC is observed in sour environments without external stresses. The internal hydrogen pressure theory is typically used to explain HIC.^{2,3,7,8} It is postulated that hydrogen atoms diffuse through the lattice and recombine as H₂ gas that accumulates at discontinuities, principally inclusion-metal interfaces. When the gas pressure increases sufficiently, voids and cracks develop and propagate. The gas pressure depends on the hydrogen content according to Sievert's law. A concept of HIC initiation was discussed by Ikeda et al.²⁻⁵ When the absorbed hydrogen concentration (C₀) from a corrosion reaction is larger than the threshold hydrogen concentration of the material (C_{th}), HIC initiates. In contrast, when the C₀ value is smaller than the C_{th} value, HIC does not initiate. Here, C_{th} is defined as the minimum hydrogen concentration required to produce HIC in the material. The relationship between the critical hydrogen concentration for HIC initiation (C_{th}) and inclusion size at HIC initiation can be derived as follows. The critical fugacity of hydrogen gas (P_{crit}) for starting an unstable crack growth at the crack tip of the pre-crack length (a_{crit}) is expressed as follows⁹:

$$P_{crit} = C_1(a_{crit})^{-1/2} \quad C_1: \text{constant} \quad (1)$$

where P_{crit} is the critical fugacity of hydrogen gas in pre-crack. Here, a_{crit} is considered to be the critical length of a non-metallic inclusion, such as an elongated MnS for HIC initiation. Sievert's law indicates the relationship between P_{crit} and C_{th}:

$$C_{th} = C_2(P_{crit})^{1/2} \quad C_2: \text{constant} \quad (2)$$

Hara et al.¹⁰ showed that C_{th}, as a critical hydrogen permeability (Per_{crit}) for HIC initiation, was expressed as a function of the critical length of inclusions (a_{crit}) and the maximum hardness of the center segregation zone (HV_{max}). After the crack initiates and propagates, a quasi-cleavage fracture surface appears. However, it is often difficult to find the true initiation site of HIC because it is not possible to follow the river pattern to find the starting point as in the case of cleavage fracture in body-centered cubic (bcc) iron at low temperatures.

Recently, sour environmental severity for HIC susceptibility was proposed based on the equi-hydrogen permeability concept.¹¹⁻¹³ Previously, several researchers had investigated the behavior of hydrogen entry for various sour environments.¹¹⁻¹⁹ These studies were conducted to obtain C₀. Then, the relationship between the severity map (obtained by hydrogen permeability and/or hydrogen content) and HIC susceptibility was investigated. After that, it was proposed that the HIC behavior corresponds well with the steady-state hydrogen permeability.¹³ These trends can be explained by in-situ HIC observation techniques and hydrogen diffusion behavior calculated using finite element analysis (FEA).²⁰

Meanwhile, several studies on in-situ HIC observation techniques were proposed to study the HIC phenomena and mechanisms in more detail by Kushida et al.²¹, Sawamura et al.²², Fujishiro et al.²³, and Yasuda et al.²⁰. The in-situ HIC measurement technique developed by Kushida et al. was based on the combination of the electrochemical hydrogen permeation method and the automatic ultrasonic wave inspection system. Therefore, the in-situ technique can make the connection between HIC propagation behavior and hydrogen permeability. On the other hand, using the in-situ HIC observation system developed by Sawamura et al., HIC testing can be conducted in accordance with NACE TM0284-2016. This in-situ system made it possible to make the connection between HIC propagation behavior and HIC susceptibility, such as crack area ratio (CAR) and crack length ratio (CLR). The in-situ system developed by Fujishiro et al. established the connection between HIC propagation behavior and the microstructure. Furthermore, the in-situ system developed by Yasuda et al. established the connection between the three-dimensional (3D) images of cracks and local hydrogen concentration. However, the HIC initiation sites have generally been predicted by ex-situ observation of steel materials after HIC tests. There is no in-situ observation technique that can make a direct connection between HIC initiation sites and inclusions.

In this study, a new in-situ HIC observation technique was developed to identify the true initiation site of HIC. The initiation time and location of HIC was identified using the developed in-situ HIC observation technique. The C-scan images were obtained by measuring the HICs at each time point using the ultrasonic system. By projecting the C-scan movie onto the EDS map of the HIC fracture surface and playing it back, as in projection mapping, the start point of HIC was identified. Then, the initiation site of HIC was related to the non-metallic inclusion directly. Additionally, the hydrogen concentration at the HIC initiation point was calculated using the finite element method (FEM) to obtain the C_{th} of the fracture.

EXPERIMENTAL PROCEDURE

Material

A low-alloy carbon steel with the chemical composition shown in Table 1 was used as a test material in this study. The slab was manufactured in a mill and contained center segregation. The slab, after being austenitized, was rolled into a 22 mm thick plate, accelerated-cooled, to obtain American Petroleum Institute (API) grade X70 (yield strength of 70 ksi (485 MPa) or higher) steel. This steel is non-sour resistant steel consisting of ferrite–bainite dual microstructure with a high manganese (Mn) content, sulfur (S) content exceeding 10 ppm, and no calcium (Ca) treatment. Table 2 shows the strength of the specimens, whereas Figure 1 shows the optical micrograph at the mid-thickness of the tested plate.

Table 1
Chemical composition of test material (wt%)

C	Si	Mn	S	Others	bal.	Remarks
0.06	0.2	1.9	0.0011	Cu, Ni, Cr, Nb, Ti, Al	Fe	Non-Ca-treatment

Table 2
Tensile strength and grade of test material

Yield strength, YS [MPa]	Tensile strength, TS [MPa]	Grade	Remarks
515	668	Non-sour	Ferrite + Bainite

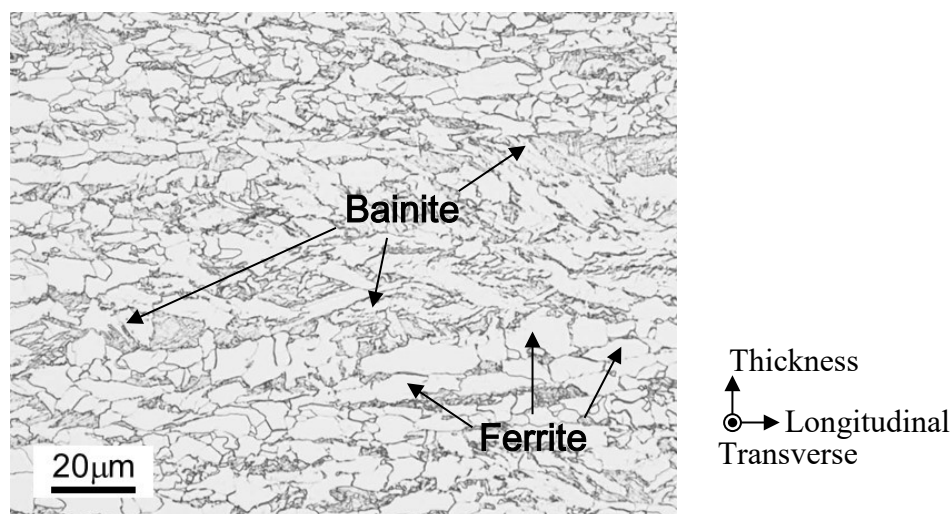


Figure 1: Optical micrograph of the tested plate at the mid-thickness.

HIC test and in-situ HIC observation

The HIC test was performed as per NACE TM0284.¹ The HIC initiation behavior was observed using an in-situ HIC observation instrument simultaneously. However, in this study, the sides of the HIC specimens were covered using a polyimide resin tape to limit the path of hydrogen penetration and to prevent hydrogen penetration from locations other than the front and back surfaces. Additionally, the test period ended when HICs were generated and the size of the fracture surface could be determined.

The test specimens, which were taken from the test material, were emery-polished down to # 320. The specimen was 15 mm thick, 20 mm wide, and 100 mm long. A highly buffered HLP solution²⁴⁻²⁹ (pH 3.0), i.e., 5wt% NaCl + 0.93 N ($\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$), was used as a test solution in the same manner as in the hydrogen permeation test. This test solution with strong buffering capacity was originally adopted by the High-strength Line Pipe (HLP) research committee at the Iron and Steel Institute of Japan (ISIJ)⁽¹⁾ as an optional HIC test solution. This test solution is currently proposed as the HLP solution for NACE TM0284-2016.²⁴⁻²⁹ Figure 2 shows the schematic drawing of the HIC specimen and the in-situ HIC observation instrument. The instrument used in this study was originally developed by Sawamura et al.²² The HIC detection system was composed of a 10 MHz ultrasonic probe at the detection side, and the detection side chamber was separated from the HIC testing side by a plastic barrier. The HIC testing side chamber was filled with the test solution (HLP solution pH 3.0), whereas the detection side was filled with water. C-scan mapping was performed automatically during the HIC test. The auto-scan was undertaken at 20 to 30 minutes intervals to observe the HIC initiation behavior. The test temperature of the solution was maintained at $25 \pm 3^\circ\text{C}$ by a water bath maintained at constant temperature.

Identification of the HIC initiation site

Using C-scan maps as the frames of a movie, a C-scan movie that shows HIC initiation behavior was prepared. Figure 3 shows the in-situ HIC observation system. After the test, specimens that were machined from the close part of HIC, which occurred around mid-thickness of tested plate, were notched, placed in liquid nitrogen (-196°C), and cut to reveal the HIC fracture surface. The HIC fracture surfaces were observed using SEM and EDS. Finally, the HIC initiation behavior obtained from the C-scan movie was overlaid with the fracture surface, similar to projection mapping, as shown in Figure 3. Figure 4 shows a schematic drawing of the procedure to identify the initiation sites of HICs. First, the HIC image of the last frame of the C-scan movie was projected onto the HIC fracture surface. Then, the C-scan movie was played backward on the HIC fracture surface, as in projection mapping, to identify the start

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points of HICs. The start points of HICs were observed by SEM/EDS and the true initiation site of the HIC (inclusions) was identified.

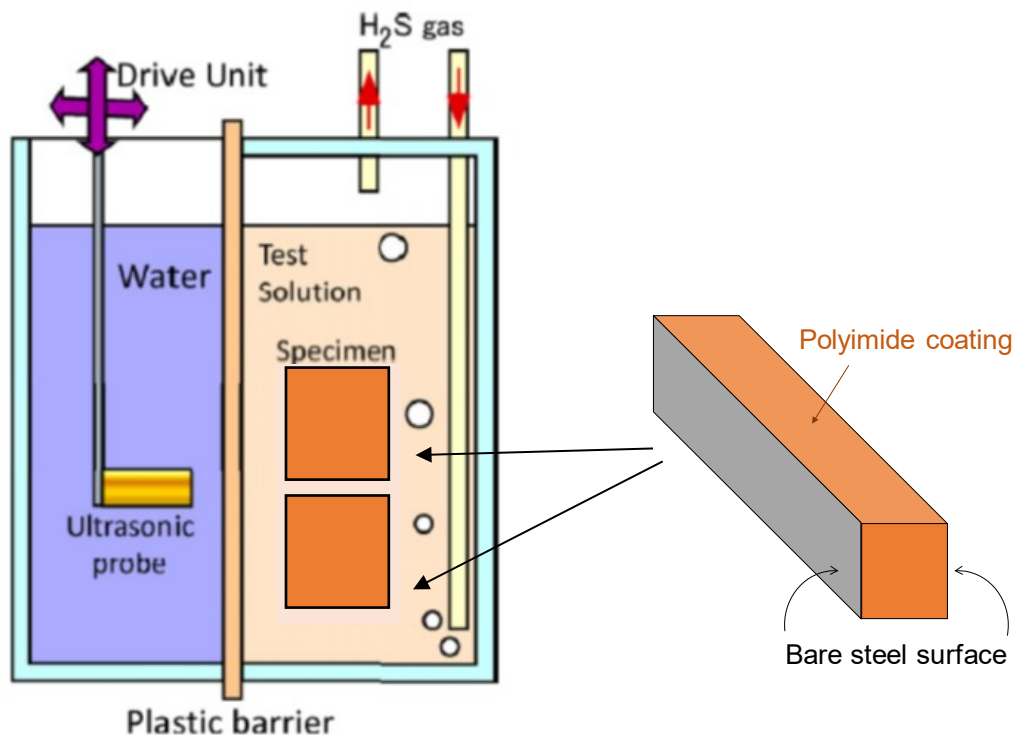


Figure 2: Schematic drawing of a HIC specimen and the in-situ HIC observation instrument.

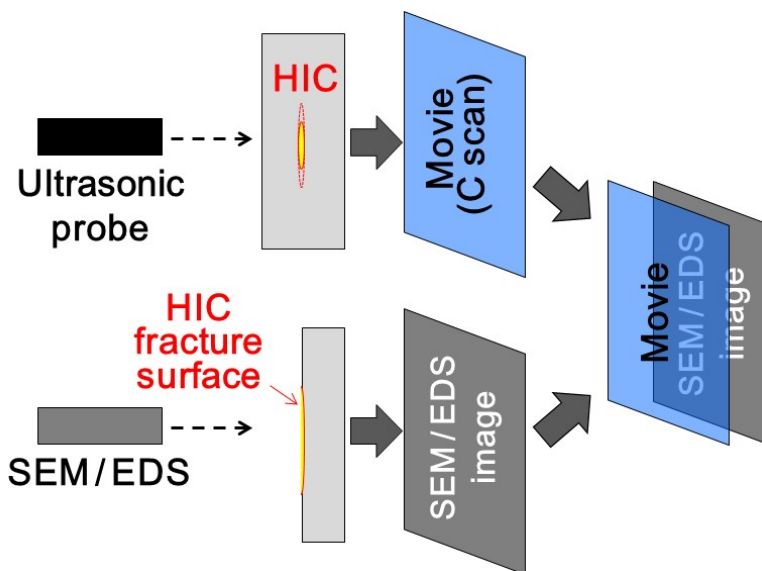


Figure 3: Schematic drawing of the in-situ HIC observation system.