

Sour Environmental Severity based on Hydrogen Permeability and HIC/SSC susceptibilities

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ABSTRACT

Hydrogen Induced Cracking (HIC) and Sulfide Stress Cracking (SSC) are major issues of line pipes exposed to sour environment. Severity of sour environment determined in accordance with EFC 16 and NACE MR0175 / ISO15156 for low-alloy steels has been proposed based on experimental SSC results. However, SSC susceptibility does not necessarily correspond to HIC susceptibility. The susceptibility of HIC and SSC, which are types of hydrogen embrittlement, would be accurately predicted if absorbed hydrogen content under every environment and critical hydrogen content are fully obtained. In this study, hydrogen permeability domains as a function of pH and H₂S partial pressure were determined. In addition, the susceptibilities to these hydrogen-assisted environmental cracking modes under various combinations of pH and H₂S partial pressure were also investigated. The severity of the sour environment was proposed based on the hydrogen permeability and the susceptibility for hydrogen assisted environmental cracking.

Key words: Sour environment, Hydrogen, HIC, SSC, Linepipe

INTRODUCTION

In oil and gas industry, oil country tubular goods (OCTG) or linepipes 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 catalytic action of H₂S. The absorbed hydrogen enhanced by H₂S affects hydrogen embrittlement. Hydrogen Induced Cracking (HIC) and Sulfide Stress Cracking (SSC) are hydrogen embrittlement caused forms of cracking occurring under sour conditions.

To evaluate susceptibility for this environmentally assisted cracking mechanisms, NACE TM0284 solution A, B, C and HLP solution, which comprises sodium chloride, acetic acid, and/or HCl dissolved in distilled water with various pH are used.¹ However, various H₂S partial pressures and pH values exist in actual oil and gas wells around the world. Therefore, corrosion tests often require solutions with H₂S partial pressure and pH close to those of actual sour environments in European Federation of Corrosion (EFC) specifications.² The severity of sour environment determined in accordance with EFC 16 and NACE MR0175 / ISO15156 for carbon and low-alloy steels has been proposed as indicated in Figure 1.^{2,3} Material properties such as yield strength and hardness are required depending on the severity of sour environment. The critical line of each region which was indicated as regions 0, 1, 2 and 3 in Figure 1 based on experimental SSC results of API grade N80 and P110.⁴ P110 is not applicable to the region below the upper diagonal (region 2 and 3) and N80 is not applicable to the region below the lower diagonal (region 3). Some researchers have investigated the susceptibility of HIC under various sour environments.^{5,6,7,8} However, HIC susceptibility does not necessarily correspond to SSC susceptibility. Hence, hydrogen assisted environmental cracking (HIC and SSC) domains as functions of pH and H₂S partial pressure have not been fully generalized.

Many researchers have investigated the behavior of hydrogen entry for various sour environments.^{5,6,9,10,11,12,13,14} HIC or SSC, which is a type of hydrogen embrittlement, occurs if hydrogen concentration entering into steel from the environment. Thus the critical line of each region should be determined based on hydrogen concentration in steel from the environment. In a precise sense, the local hydrogen concentration at the crack tip of the HIC or SSC should be evaluated. However, it is so difficult to evaluate the local hydrogen concentration because the local hydrogen concentration is affected by both environmental factors and material factors, such as a hydrogen diffusion coefficient of steels.

In this study, the relationship between the severity map obtained by hydrogen permeability and HIC/SSC susceptibility was investigated. The hydrogen permeability is widely used as an index instead of the hydrogen concentration and it is reported that the hydrogen permeability is not affected by material factors but affected by environmental factors.^{15,16} Therefore, the hydrogen permeability should be an index that evaluates the environmental severity for sour service. A hydrogen permeation system has been adjusted carefully and maximum values and steady-state values of hydrogen permeability were measured, under various sour environments. Using the hydrogen permeability, the severity of sour environment was proposed. In addition, the susceptibilities of these hydrogen assisted environmental cracking modes under various pH and H₂S partial pressure were also evaluated. This paper describes the relationship between the experimental severity maps obtained by the hydrogen permeability and HIC/SSC susceptibility.

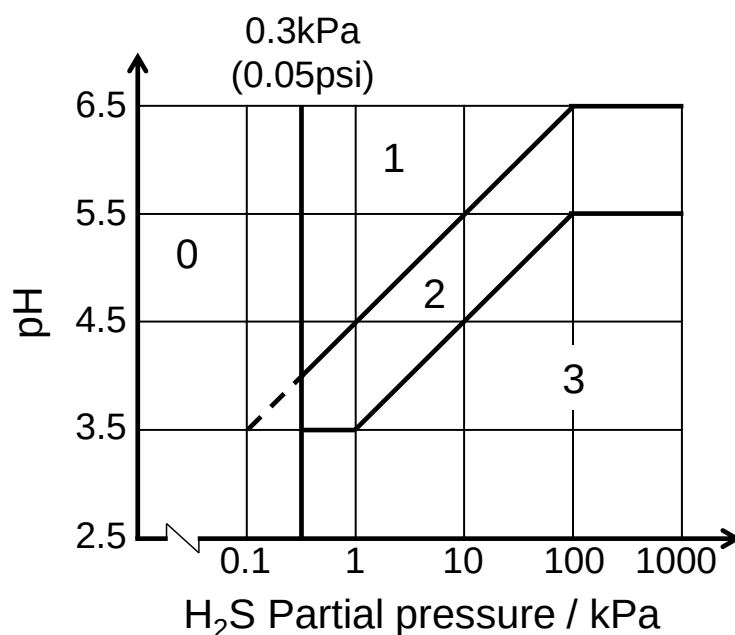


Figure 1: Regions of environmental severity with respect to the SSC of carbon and low-alloy steels.³

EXPERIMENTAL PROCEDURE

Material

The low-alloy carbon steels with a chemical composition given in Table 1 were used in this study. Steel 0 was melted in a laboratory and linepipe steels 1 to 4 were manufactured in actual mills. These steels, after being austenized, were rolled into 15 to 25 mm thick plates and accelerated-cooled in order to obtain X65 to X80 grade bainitic microstructure, as shown in Figure 2. Figure 2 shows an example of scanning electron micrograph at quarter-thickness of the 16-mm-thick plate for Steel 0 on the longitudinal-thickness cross section. The Steel 0 which was melted and rolled in a laboratory was used as a test material for hydrogen permeation in this study. The test specimens, with dimensions of 1 x 40 x 40 mm for hydrogen permeation test, were taken from the quarter-thickness of the 16-mm-thick plate. The Steels 1 to 4 with center segregation which were manufactured in mills were used as test materials for HIC tests. Table 2 shows tensile strength and grade of tested materials. The Steel 4 is a sour resistant bainitic steel with X65 grade and the others are non-sour resistant bainitic steels with X65 to X80.

Table 1
Chemical composition of tested materials for hydrogen permeation, HIC, and SSC tests (wt%)

Steel	C	Si	Mn	Others	bal.	Remarks
0	0.05	0.2	1.5	0.07 (Nb+Ti+Al)	98 (Fe)	Hydrogen permeation test
1	0.04 ? 0.06	0.1 ? 0.3	1.3 ? 1.9	0.1	98	HIC test, SSC test
2				?	?	HIC test
3				2.0	95	
4				[Cu+Ni+Cr+Mo +Nb+Ti+Al]	(Fe)	

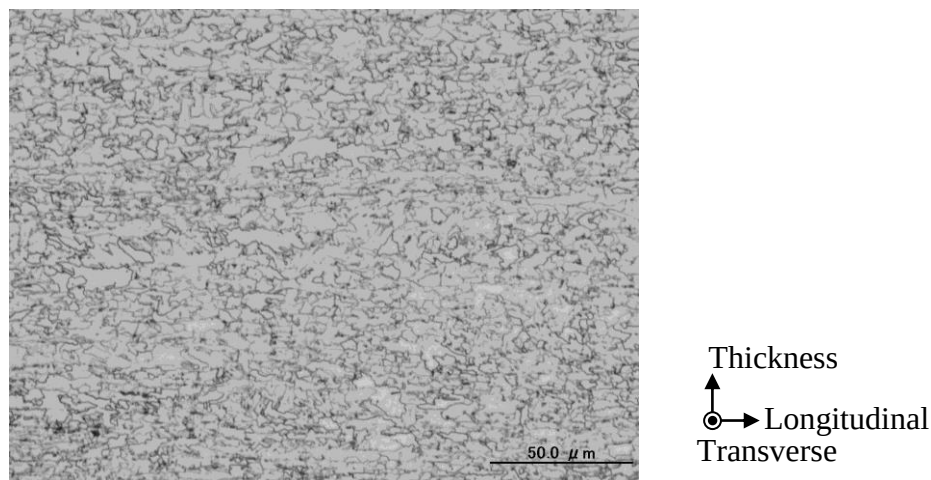


Figure 2: Scanning electron micrograph at quarter-thickness of the 16-mm-thick plate (Steel 0).

Table 2
Tensile strength and grade of tested materials for hydrogen permeation, HIC, and SSC tests

Steel	TS [MPa]	Grade		Remarks
0	586	X65	-	Hydrogen permeation test
1	761	X80	Non-sour	HIC test, SSC test
2	682	X70	Non-sour	HIC test
3	564	X65	Non-sour	
4	582	X65	Sour	

Test solutions

HLP solution (5wt% NaCl + 0.93N CH₃COOH/CH₃COONa), was used as the test solution, in order to maintain solution pH value. This test solution with strong buffering capacity was originally adopted in the High-strength line pipe (HLP) research committee in the Iron and Steel Institute of Japan (ISIJ)⁽¹⁾ as an optional HIC test solution and is currently proposed as HLP solution for NACE TM0284-2016.^{17,18,19,20,21} The initial pH of the test solution was adjusted to the target pH ± 0.2 pH units by mixing 5.0 wt% NaCl + 0.93 N CH₃COOH and 5.0 wt% NaCl + 0.93 N CH₃COONa. Test solution was deaerated with nitrogen gas for 24 h and purged with H₂S-CO₂ mixed gas before the hydrogen permeation test. After purging, H₂S-CO₂ mixed gas was also bubbled through the test solution during the hydrogen permeation test. Table 3 shows the list of test solutions for hydrogen permeation, HIC, and SSC tests.

Hydrogen permeation method

Hydrogen permeability and corrosion potential were measured using an electrochemical hydrogen permeation method with nickel-plated specimens on the anode-side surface.²² In this study, hydrogen permeation system and experimental methodologies were carefully adjusted at two different sites, in order to obtain appropriate values of hydrogen permeability. The test solution pre-purged with H₂S-CO₂ mixed gas was used and H₂S-CO₂ mixed gas was also bubbled through the test solution during the hydrogen permeation test in both a laboratory A and a laboratory B. In addition, all experimental procedures and conditions for deaeration, H₂S-CO₂ mixed gas purging, and Ni-plating were also adjusted in both a laboratory A and a laboratory B. Glass cells that have same shape and polyvinyl chloride tubes that have same composition were used in both a laboratory A and a laboratory B. After these adjustments, hydrogen permeation tests were conducted once under various pH and H₂S partial pressure in a laboratory A and a laboratory B in the same way. Other adjusted procedures were as

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