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Effect of H_2S Partial Pressure and pH of Test Solution on Hydrogen Induced Cracking of High Strength Low Alloy Steels

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Hydrogen induced cracking (HIC) is one of the hydrogen degradation phenomena of linepipe steels caused by H_2S gas in the crude oil or natural gas. However, NACE TM0284-96 standard HIC test method is hard to satisfy the steel requirements for sour service application since it uses more severe environmental conditions than actual conditions. Therefore, in order to use steels effectively, it is required to evaluate HIC resistance of steels in the practical range of environmental severity.

In this study, HIC resistance of two high strength low alloy (HSLA) steels being used as line pipe steels was evaluated in various test solutions with different H_2S pressures and pH values. The results showed that the key parameter affecting crack area ratio (CAR) is H_2S partial pressure of test solution when the pH value of test solution is not over 4. Hydrogen diffusivity was not a constant value, but it was rather affected by the hydrogen ion concentration (pH value) in the solution.

Keywords : *Hydrogen induced cracking (HIC), HSLA steel, pH, H_2S partial pressure, hydrogen.*

1. Introduction

HIC is a kind of the hydrogen embrittlement which occurs in the form of surface blisters and/or internal cracks in the absence of applied stress. Susceptibility of steels to HIC is closely related with metallurgical parameters, especially distribution of defects such as non-metallic inclusions and secondary phases. The environment to which steels are exposed is also another important parameter affecting HIC of steels. The test environment of NACE TM0284-96 standard HIC test method is unnecessarily severe than that of actual sour service conditions. In order to use linepipe steels properly according to actual service environments, it is required to evaluate HIC resistance of steels in the practical range of environmental severity. The environmental factors critically affecting HIC are considered to be 'pH level and H_2S partial pressure of in-service environments' because both the pH and H_2S partial pressure affect the diffusion of hydrogen atoms in steels. It has been reported that hydrogen permeation rate (HPR), which is closely related with HIC, increases with decreasing pH of the environments.[1)] However, hydrogen concentration in steels predominantly depends on the H_2S partial pressure of environments while the influence of the pH is less important.[2)]

In this study, the effect of pH and H_2S partial pressure of test solution on HIC resistance of two commercial HSLA steel plates at various environmental severities was studied in terms of hydrogen diffusion and metallurgical parameters such as microstructure and inclusion.

2. Experimental procedure

2.1 Specimens and HIC test

The specimens used in this test were two commercial HSLA steel plates which belonged to API X70 grade according to API 5L specification. Each steel plate was produced by different steel making process. The difference in chemical composition between two steels is carbon content; 0.03wt% (Steel A) and 0.05wt% (Steel B). Hereafter, two different steels will be identified as steel A and steel B. HIC tests were performed for 96 hrs in 9 different kinds of test solutions, and the solution chemistries are listed in Table 1. After HIC testing, cracking sensitivity

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Table 1. Test solution chemistry.

Chemistry \ Solution no	1	2	3	4	5	6	7	8	9
H_2S(atm)	1	1	1	0.1	0.1	0.1	0.01	0.01	0.01
pH	2.7	4.0	5.0	2.7	4.0	5.0	2.7	4.0	5.0

was measured in terms of CAR by using ultrasonic detector.

The microstructural details of tested steels such as shape, size and distribution of inclusions were investigated using scanning electron microscopy (SEM). After HIC testing, HIC were also analyzed using optical microscopy (OM) and SEM in order to examine crack initiation and propagation. To define the chemical composition of inclusions which act as HIC nucleation sites, energy dispersive spectroscopy (EDS) was used.

2.2 Electrochemical hydrogen permeation test

Hydrogen permeation tests were conducted in a dual cell called "modified Devanatan-Stachurski cell" as shown in Fig. 1.[3] This cell is composed of two compartments - a hydrogen generating cell (input side) and a hydrogen oxidizing cell (detection side). In the hydrogen input side, hydrogen atoms enter the specimen surface by diffusion while the amount of hydrogen diffused from input side is measured in term of oxidizing current density in the hydrogen detection side. The input side is filled with NACE TM 0284 - 96A solution and potential is not applied. On the other hand, the detection side is filled with 0.1N NaOH solution and overvoltage of 250 mVSCE is applied in order to oxidize the diffused hydrogen. The thin Pd layer was electroplated on detection side of specimens in $PdCl_2$ 5.08g + NH_4 OH 1L solution.[4] Amount of the diffused hydrogen flux was measured by the hydrogen oxidation current density.

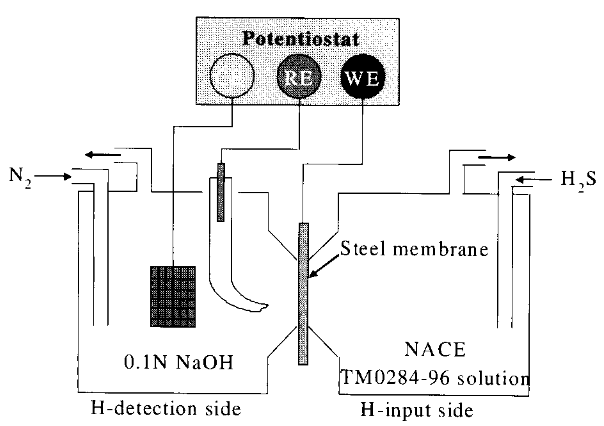


Fig. 1. Modified Davanathan-Stachurski cell

Hydrogen diffusivity in steels can be determined by breakthrough time method or relaxation time method.[5] In this study, breakthrough time method was used to determine hydrogen diffusivity for the tested steels and the relationship between the diffusivity (D), thickness of specimen (L) and breakthrough time (tb) is as follows;

$$D_b = 0.76 L^2 / \pi^2 t_b \quad (1)$$

Hydrogen permeation tests were performed only for the steel which exhibited HIC according to severity of testing environments since one of the objectives in this study was to investigate the effect of hydrogen diffusion on HIC level (in terms of CAR) of tested steels according to severity of testing environments.

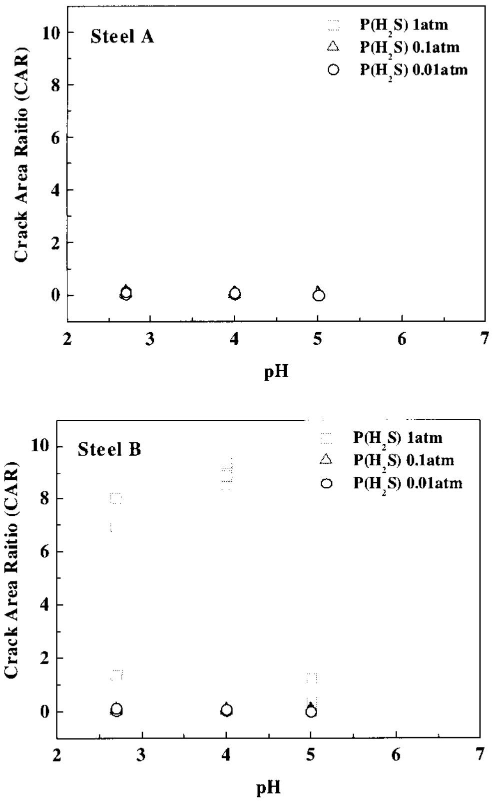
3. Result and discussion

3.1 HIC Resistance

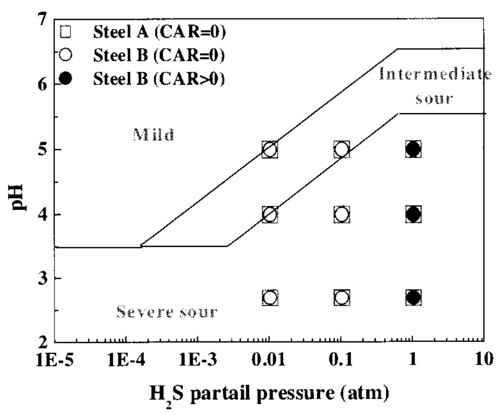
After HIC testing, cracking sensitivity was measured in terms of CAR by an ultrasonic detector.

Fig. 2 shows the effect of H_2S partial pressure and pH of test solution on HIC resistance of two different steels (CAR value). It should be noted from Fig. 2(a) that the key parameter affecting HIC is not pH value of test solution but H_2S partial pressure. Environmental severity was basically defined as proposed in the literature.[6] It was overlapped with the current HIC test result as presented in Fig. 2(b). This shows the practical application range of environmental severity for two steels. As shown in Fig. 2(b), HIC did not occur in Steel A even at the most severe condition (pH 2.7, P_{H2S} 1atm) while HIC occurred in Steel B at some conditions of severe sour region.

Fig. 3 shows microstructural characteristics of tested steels. In Figs. 3(a), 3(b), 3(c) and 3(d), steel A has a typical ferrite-pearlite microstructure including pearlite or degenerated pearlite (DP) second phases while steel B includes hard microstructures such as martensite austenite (MA) and bainitic ferrite (BF) in ferrite base. As is presented in Fig. 3(e), the size distribution of inclusions located at t/4 (t: the thickness of steel plate) of two steels was investigated because HIC occurred at that position. However, the distribution of inclusions in both steel A and B is similar. The difference in HIC resistance between two kinds of steels seems to be due to the difference of microstructures in the steels. This fact was proved by fractography analysis.



(a)

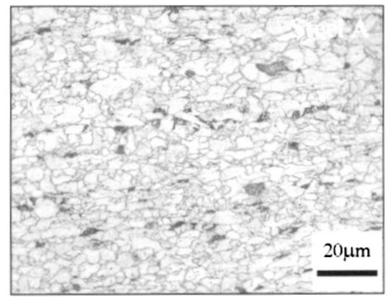


(b)

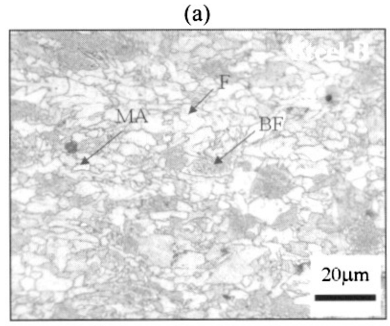
Fig. 2. HIC resistance with pH and H_2S partial pressure; (a) Effect of pH and H_2S partial pressure on HIC, and (b) Discrimination of environmental severity.

3.2 Cracking initiation and propagation

Large inclusions such as elongated manganese sulfides and clusters or stringers of oxides increase the HIC susceptibility of steels.[7] In steel making technology, Ca treatment is necessary to control the shape of such inclusions.[8),9] HIC occurred only at t/4 position of the Steel B and initiated at a single inclusion and/or at a clusters of oxide-



(a)



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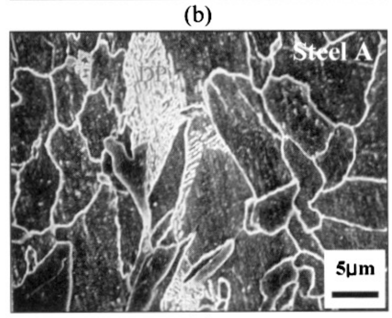
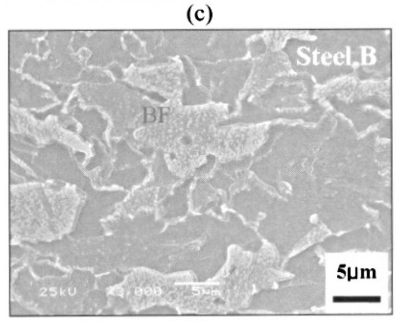


(c)



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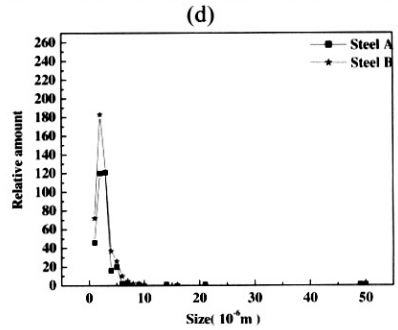
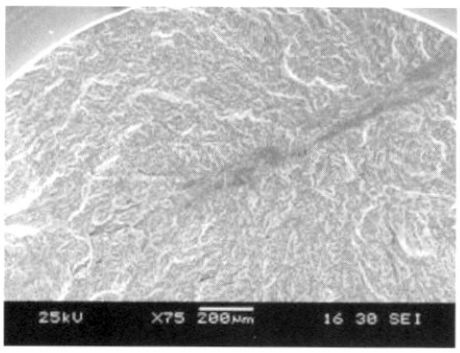


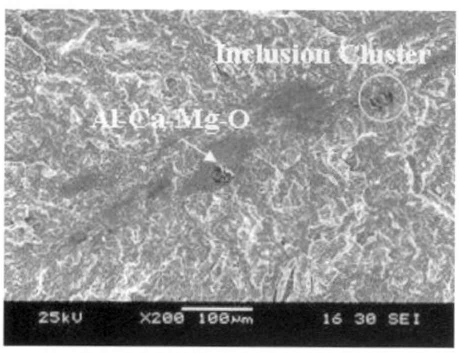
(e)

Fig. 3. Microstructures and size distribution of inclusions of two different specimens; (a), (b), (c), (d) OM and SEM micrographs showing microstructure at t/4 position of two steels, and (e) size distribution of inclusions at t/4 position of two steels.

inclusions. Fig. 4(a) and Fig. 4(b) show the HIC fracture surface which reveals typical crack initiation and propagation in Steel B. The size of a single inclusion and/or a cluster of oxide-inclusions, which acts as crack nucleation site, is over about 20 μm in maximum length. Furthermore, Figs. 4(c) shows that BF as well as inclusions is detrimental to HIC. Cracks propagated through the ferrite grain boundaries (FGB) in quasi-cleavage manner following to hard microstructures such as MA, BF as presented in Fig. 5.



(a)



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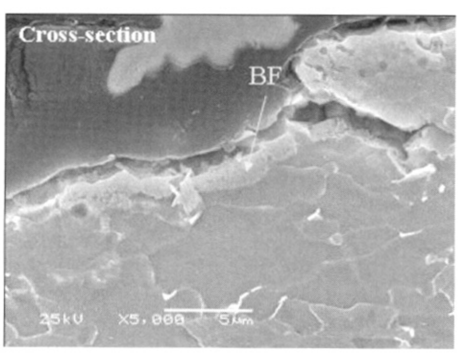
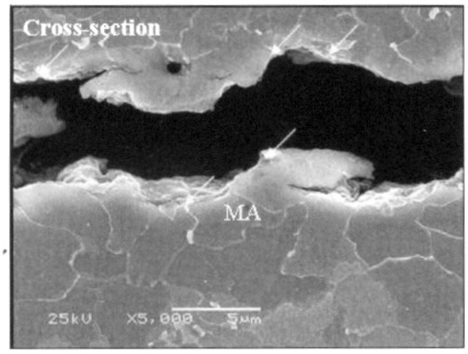
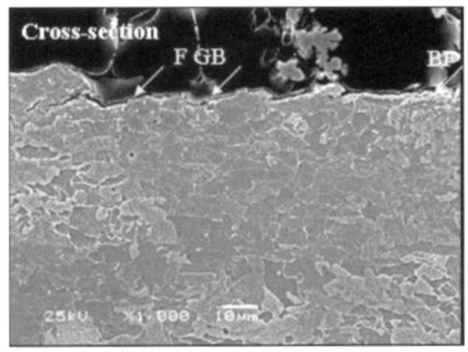


(c)

Fig. 4. The observation of HIC fracture surface; (a) and (b) Typical HIC initiation and propagation, (c) BF surrounding HIC initiation points.



(a)



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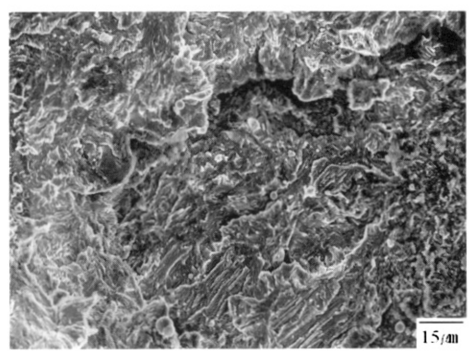

(c)

Fig. 5. The observation of cross-section of fractured specimen showing HIC; (a) HIC propagation following to MA, (b) HIC propagation following to FGB and BF, (c) HIC propagation in quasi-cleavage manner.

3.3 Hydrogen diffusion in steel

Hydrogen diffusion in steel is influenced mainly by two factors. One is the concentration of hydrogen at the steel surface and the other is hydrogen trapping sites in the steel. Trapping sites are various defects such as solute atoms, vacancies, inclusions, and precipitates in steel. It is reported that HPR, which is closely related with HIC, increases with decreasing pH of the solution.[1] However, hydrogen concentration in steel depends predominantly on the H_2S

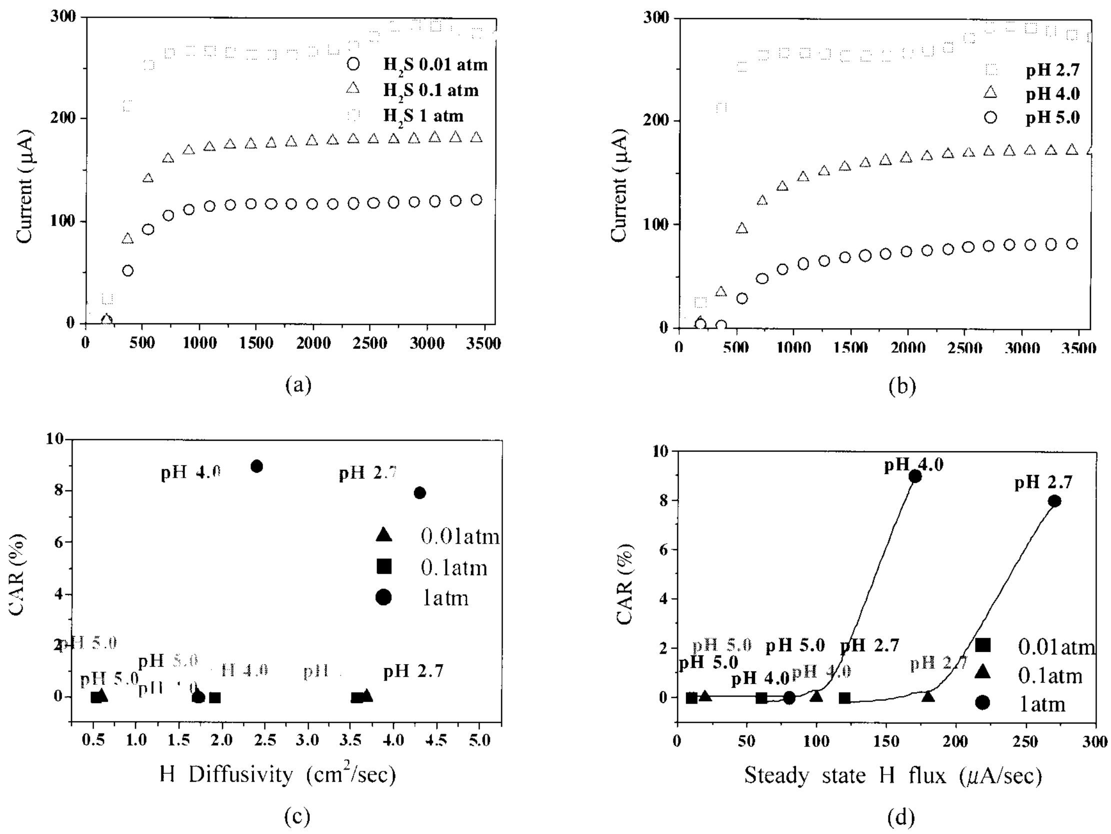

Fig. 6. Hydrogen permeation test results; (a) Hydrogen permeation curve showing the effect of H_2S partial pressure at pH=2.7, (b) Hydrogen permeation curve showing the effect of solution pH at P_{H2S}=1atm, (c) Effect of solution pH and H_2S partial pressure on hydrogen diffusivity and HIC resistance of steels (d) Effect of solution pH and H_2S partial pressure on hydrogen flux and HIC resistance of steels.

partial pressure of environment while the influence of the pH is negligible.[2)] In this paper, hydrogen permeation test was performed to investigate the effect of environmental severity on hydrogen diffusion and HIC resistance of tested steels.

In Fig. 6(a), hydrogen permeation current density at steady state increases with decreasing pH and increasing H_2S partial pressure. Fig. 6(c) shows the effect of hydrogen diffusivity and flux on average CAR values of Steel B. The diffusivity was calculated by Eq. (1). Hydrogen diffusivity was affected mainly by pH values of solution but not by H_2S partial pressure as shown in Fig. 6(c). This means that hydrogen diffusivity is not a constant value, but it is rather affected by the hydrogen ion concentration in the solution. Amount of hydrogen atoms diffusing through steels, however, was determined by both the pH value and H_2S partial pressure as shown in Figs. 6(a) and 6(b). Tables 2 and 3 summarize the effects of H_2S partial pressure and pH of test solution on hydrogen diffusion behavior through Steel B. From the fact that average CAR value is over '8' only when H_2S partial pressure is 1atm and pH values are 2.7 and 4.0 from Fig. 6 (d), critical hydrogen flux and diffusivity for CAR value over '8' are 170 $\mu A/cm^2$ and $2.4x10^{-6} cm^2/s$, respectively, as shown in Tables 2 and 3. Nevertheless, experimental conditions which exhibited higher hydrogen flux and diffusivity values than the ones for critical CAR value '8'

Table 2. Steady state hydrogen flux

Steady state H flux ($\mu A/cm^2$)		H_2S partial pressure		
		0.01	0.1	1
pH	2.7	120	180	270
	4.0	60	100	170
	5.0	10	20	80

Table 3. Hydrogen diffusivity

H diffusivity ($10^{-6}cm^2/sec$)		H_2S partial pressure		
		0.01	0.1	1
pH	2.7	3.68	3.57	4.29
	4.0	1.72	1.91	2.40
	5.0	0.60	0.53	1.72

did not induce the HIC as shown in Tables 2 and 3. This data scattering means that HIC susceptibility is affected more by H amount trapped in steels than by H flux diffusing through steels.

4. Conclusions

The effect of pH and H_2S partial pressure of test solution on HIC resistance of two commercial HSLA steel plates at various environmental severities was studied in terms of hydrogen diffusion and metallurgical parameters such as microstructure and inclusion.

The results showed that the key parameter affecting HIC is H_2S partial pressure, but not pH value of test solution. However, diffusible hydrogen flux was determined by both pH value of solution and H_2S partial pressure and could not directly determine HIC resistance of steels. This means that H amount trapped in steels is more important than H flux diffusing through steels to HIC.

Also, a single oxide-inclusion and/or a cluster of oxide-inclusions in steels acted as crack nucleation site only when BF surrounds the inclusions in some conditions of severe sour region. Cracks propagated through the ferrite grains in quasi-cleavage manner following to hard microstructures such as MA and BF.

Hence, BF is detrimental to both nucleation and propagation of HIC and the removal of it in steels will improve HIC resistance.

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