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NEAR NEUTRAL pH SCC OF GRADE X80 LINEPIPE STEELS UNDER CYCLIC LOADING

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ABSTRACT

Susceptibility to stress corrosion cracking (SCC) of Grade X80 linepipe steels, which were produced by recent TMCP (Thermo-Mechanical Controlled Processing) technique, controlled rolling (CR) followed by accelerated cooling process (ACC), in near neutral pH conditions was investigated, and cracking behavior was compared with conventional Grade X65 linepipe. Longitudinal strip specimens with small surface notches were cyclically loaded in the NS4 solution with cathodic polarization of -1000mV vs. SCE. No significant difference in susceptibility to SCC was found between Grades X80 and X65 linepipes, both produced by TMCP process, even under higher stress condition for X80 linepipe steel. Hydrogen permeation test reviled the strong effect of hydrogen for the cracking under the SCC test condition. Transgranular cracking and quasi-cleavage fracture were observed as an evidence of the effect of both corrosion and hydrogen embrittlement on near neutral pH SCC.

1. INTRODUCTION

Corrosion related material failure, such as stress corrosion cracking (SCC), is the largest cause of pipeline accidents [1, 2]. Stress corrosion cracking on the external surface is influenced by the combined conditions of corrosive environment, stress field caused by internal operation pressure and external force, and material resistance to cracking. Ground water reaches to the pipe surface in the portion where the coating material deteriorated and disbonding of the coating from pipe surface occurred. Electro-chemical reaction between pipe surface and soil water, which has various conditions depending on soil chemistry, coating material and so on, causes cracking when the pipe surface is exposed to the specific cathodic potential associated with cathodic protection of the system.

External SCC failure is classified into two types depending on morphology of the cracking and pH of the corrosive environment [3]. A significant number of traditional pipes were suffered by intergranular cracking. This type of failure is caused in carbonate-bicarbonate solution with high pH of around 9 to 12, and localized dissolution process enhanced by grain boundary segregation and repeated rupture of passive films in the crack tip causes extension of intergranular cracking [4-6]. It was suggested that microstructure of the steel has strong effect on the intergranular cracking, and steels with homogeneous microstructure showed higher resistance to the high pH SCC [7]. On the other hand, SCC failure by transgranular cracking was reported in more recent pipelines under near neutral pH condition of around 5 to 8 [8-10]. Macroscopic features of near-neutral pH SCC are described as below [11];

- Presence of numerous surface cracks and linking up to form long crack.
- Similar form of cracking as stress corrosion fatigue that requires cyclic loading.
- Wide, straight and transgranular crack path with little branching.

Although the precise mechanism has not been revealed, near neutral pH SCC is considered to be strongly influenced by corrosion fatigue and hydrogen embrittlement [12-15]. In order to evaluate resistance to near neutral pH SCC, several testing methods were developed. Those testing were conducted under the loading conditions of either slow strain rate [14,16] or cyclic loading [17-19]. Different kinds of testing methods should be conducted for fully understanding of the mechanisms of near neutral pH SCC. Cyclic loading testing by the specimen with surface notches is one of the methods that can evaluate susceptibility to SCC in terms of the crack initiation [18].

While many of investigations were conducted using the conventional grade linepipes, such as API Grade X65, higher strength grade linepipes are required in the recent pipeline for increasing operation pressure and reducing material and construction cost, and application of Grade X80 linepipes were increasing. In the previous work [18], Grades X65 and X80 linepipes produced by TMCP process and having bainitic

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* This work was done as a research activity of High Strength Linepipe (HLP) Research Committee of the Iron and Steel Institute of Japan.

microstructure, showed higher resistance to SCC than the lower grade 5LB and X65 linepipes with ferrite-pearlite microstructure. However, because of the limited experimental data, reliability of recent high grade linepipe steel against near neutral pH SCC has not yet been ensured. In this paper, susceptibility to SCC of grade X80 linepipes was investigated by the cyclic loading testing with cathodic polarization. In order to ensure the reliability of the test data, three X80 linepipes from different pipe manufacturer were used and SCC test was conducted in different testing firms. Hydrogen permeation testing and precise investigation of the cracking were also conducted to investigate the mechanism of the cracking.

2. EXPERIMENTAL PROCEDURES

2.1 Materials

Chemical compositions of grades X80 and X65 linepipes are shown in Table 1. Low C microalloyed steels with slight difference in alloying elements were used. Steel plates were manufactured by applying TMCP process, controlled rolling followed by accelerated cooling, and pipes were made by UOE process and longitudinal seam welding by SAW (submerged arc welding). Table 2 shows size and mechanical properties of the linepipes. Pipes A, B and C were Grade X80 linepipes and these linepipes were produced by three different pipe manufacturer. Tensile properties were measured by API full thickness strip specimen. All pipes have sufficient strength for grade X80 and X65.

Table 1 Chemical compositions of the linepipes used.

No	C	Si	Mn	P	S	others	Ceq
A	0.07	0.10	1.85	0.006	0.0008	Cu, Ni, Mo, Nb, Ti	0.45
B	0.06	0.15	1.80	0.008	0.002	Cu, Ni, Mo, Nb, V, Ti	0.45
C	0.09	0.22	1.85	0.007	0.0018	Mo, Nb, Ti	0.41
D	0.08	0.09	1.54	0.010	0.002	Nb, V, Ti	0.36

Table 2 Mechanical properties of the linepipes used.

No	Grade	Pipe size		Direction	API strip specimen			SCC specimen	
		OD (mm)	WT (mm)		YS (MPa)	TS (MPa)	EL (%)	YS (MPa)	TS (MPa)
A	X80	1219	14.3	Trans.	608	740	34	-	-
				Longi.	592	730	31	658	699
B	X80	1067	19.3	Trans.	571	731	34	-	-
				Longi.	604	705	36	653	723
C	X80	762	19.0	Trans.	630	729	36	-	-
				Longi.	573	715	40	617	686
D	X65	508	20.5	Trans.	490	620	41	-	-
				Longi.	464	582	43	541	595

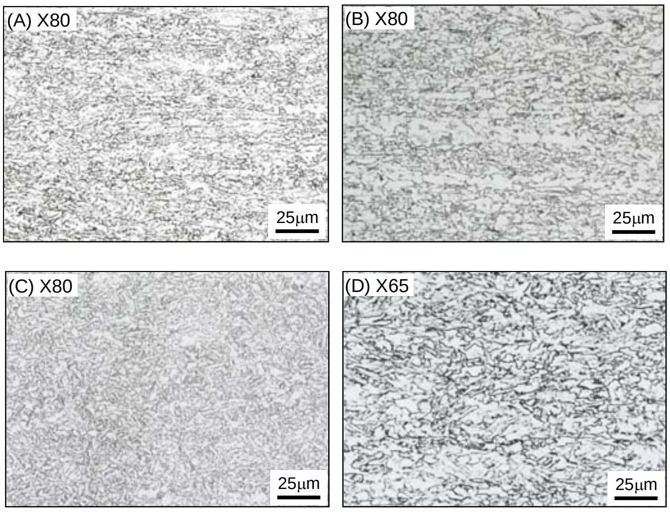


Figure 1 Microstructure of the linepipes used for the test.

Microstructure of the linepipes in the quarter thickness portion is shown in Figure 3. All steels have the microstructure with bainite and bainitic ferrite, but X65 shows relatively higher fraction of bainitic ferrite.

2.2 SCC test specimen

SCC specimens were taken from the outer surface region of the pipes in the longitudinal direction. Figure 2 shows the configuration of the SCC test specimen. One side was ground and polished to 320 grit (polished side), while mill scale of the pipe outer surface was remained in the opposite side (mill scale side). Six surface notches, four 0.3mm depth notches, one 0.2mm depth notch and one 0.1mm depth notch, were introduced on both polished and mill scale sides. Detail of the notch configuration was also shown in Figure 2. Surface

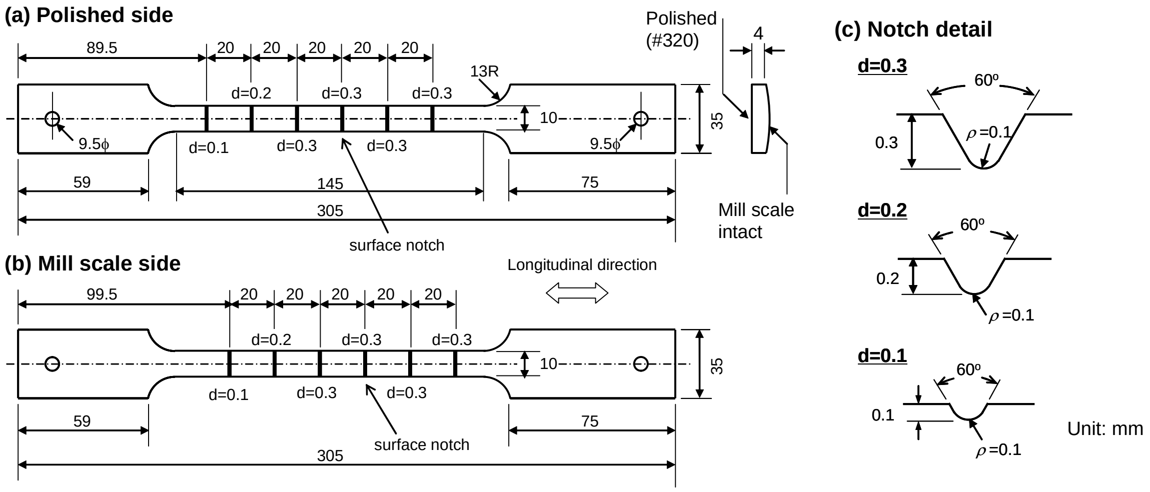


Figure 2 Configuration of the SCC specimen

notches are considered to become an initiation site for SCC cracking because of stress and strain concentration around notch tip. However, it was verified by FEM analysis that strain concentration around the notch is not so large for ductile crack initiation.

Tensile test by using SCC specimen without surface notches was conducted in order to specify loading conditions in the SC test. YS and TS are shown in Table 2. Yield strength measured by SCC specimen was higher than that obtained by full thickness API specimen, since surface region of the pipe usually has higher strength because of higher cooling rate in accelerated cooling process and higher plastic strain induced in pipe forming process. Applied stress in the SCC test was decided based on YS by SCC specimen.

2.3 SCC test conditions

Cyclic loading test was carried out using the above mentioned SCC specimen with the notch region soaked in the NS4 solution [14] as shown in Figure 3. Composition of the NS4 solution is shown in Table 3. After setting the specimen in the test cell and filling the solution into the cell, mixed gas of 10%CO_2 and 90% N_2 was injected and saturated. The test was conducted at ambient temperature of around 25°C. The test specimen was polarized to cathodic potential of -1000mV vs. saturated calomel electrode (SCE) using potentiostat and a Pt counter electrode. It should be noted that cathodic potential for this SCC test was intentionally increased in order for promoting cracking in SCC test because previous work showed no cracking in X80 linepipe under conventional cathodic protection condition of -850mV. Then, cyclic stress of triangle wave was applied 30 minutes after applying cathodic charge. Maximum applied stress was 100% of actual YS, which was measured by SCC specimen. Stress ratio, the ratio of minimum stress to maximum stress, was 0.5. The loading rate was around 980N/min and test duration was 4 weeks. There was no significant change in pH of the solution during the test; pH was around 6.5 for all tests. Testing conditions and loading condition were summarized in Table 4 and Figure 4.

In order to ensure the test results, above mentioned SCC test was conducted in three different testing firms by using the same pipe samples. After finishing the SCC test, notch root surface was observed by SEM (scanning electron microscopy) in order to investigate crack initiation from the surface. Then, the specimen was cut in the centerline and cross section was observed by optical microscopy. For the determination of crack initiation, surface observation results were used because there is a possibility of missing cracks when cutting the specimen.

Table 3 Compositions of SCC test solution

Type	compositions (g/L)			
	KCl	$NaHCO_3$	$CaCl_2 \cdot 2H_2O$	$MgSO_4 \cdot 7H_2O$
NS4	0.122	0.483	0.181	0.131

Table 4 Standard SCC test conditions.

Items	Conditions
Solution	Type NS4 by Parkins
Temperature	25°C
Gas	10%CO_2 + 90%N_2
Cathodic Potential	-1000mV vs. SCE
Maximum Stress (σ_{max})	100% Actual YS
Stress Ratio (R)	0.5
Test Duration	4 weeks

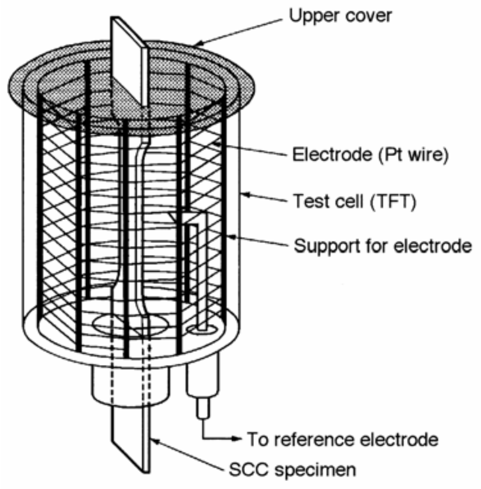


Figure 3 SCC test cell with specimen.

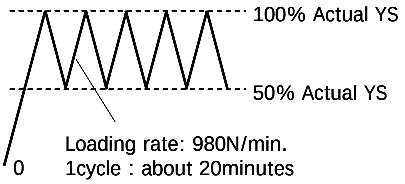


Figure 4 Loading condition in the SCC test.

2.4 Hydrogen permeation measurement

Hydrogen permeation test was conducted in order to investigate the hydrogen effect under the SCC test environment. Thin plate specimen with 1.0mm thick was extracted from the pipes No. A and D in Table 2, and hydrogen permeation rate was measured by electro-chemical method [20]. The specimen was Ni plated and one side was exposed to the same environment as the SCC test, i.e. NS4 solution with cathodic polarization of -1000mV vs. SCE. The other side of the specimen was connected to the cell with NaOH solution and current caused by hydrogen permeation was measured.

3. RESULTS OF THE SCC TEST

After 4 weeks SCC test under cyclic loading with cathodic charge, crack initiation behavior from the notch root region was investigated by SEM observation. Figure 5 shows SEM microphotographs of notch root surface of Pipe A (X80) specimen in the different notch depth. No crack initiation was found in the 0.1mm depth notch, but, several small cracks were formed and linked to large crack in the 0.3mm depth notch. In the 0.2mm depth notch, cracks were found only in mill scale side. Figures 6 and 7 show SEM microphotographs of Pipes B and C specimen, respectively, in the 0.3mm depth notch. Both specimens show cracking with linking of multiple small cracks in the notch root region. It can be stated that crack initiation behavior of reported near neutral pH SCC was simulated by the SCC test method applied in this paper.

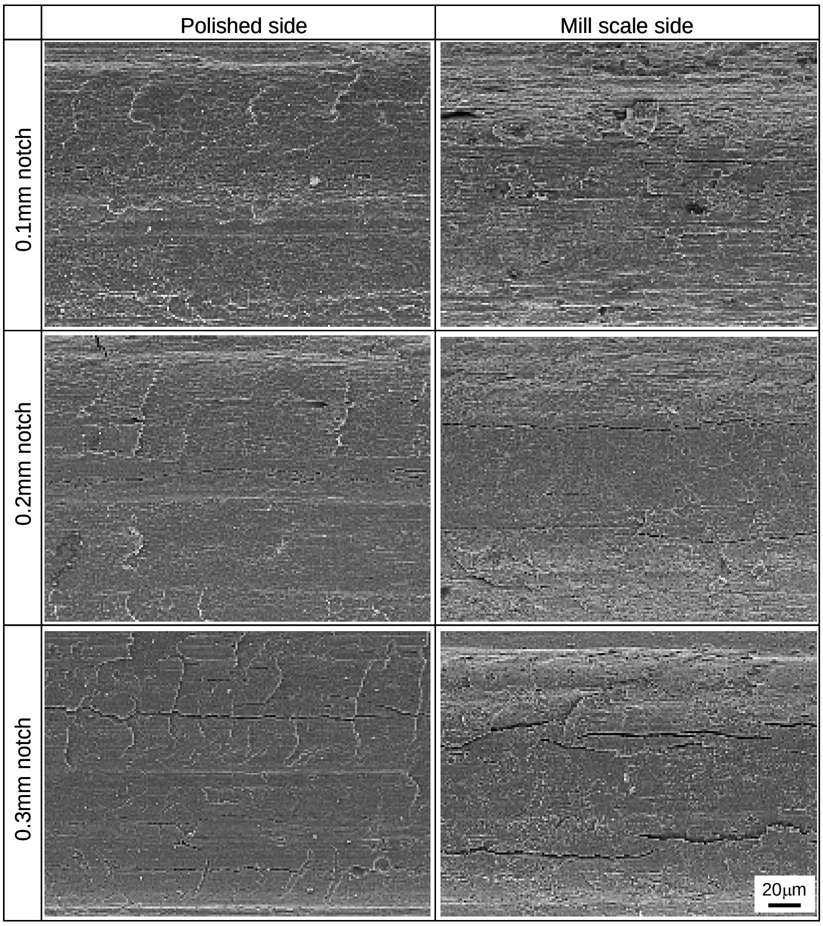


Figure 5 SEM micrographs of notch root surface of Pipe A (X80) specimen after the SCC test.

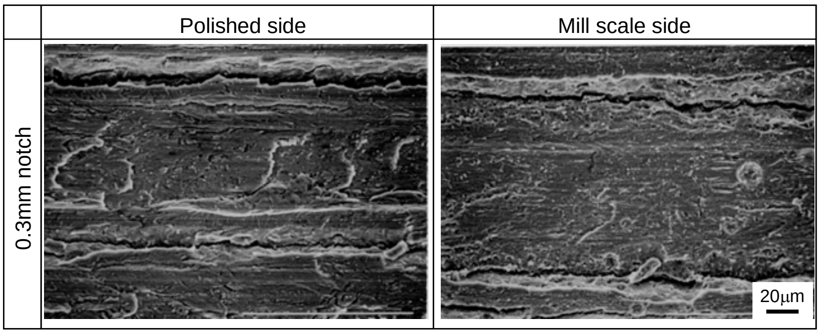


Figure 6 SEM micrographs of notch root surface of Pipe B (X80) specimen after the SCC test.

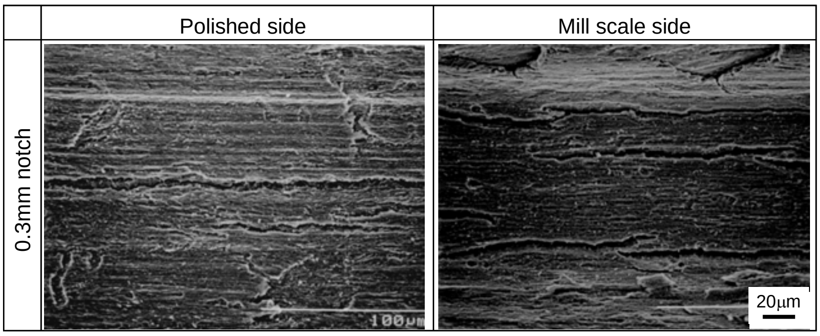
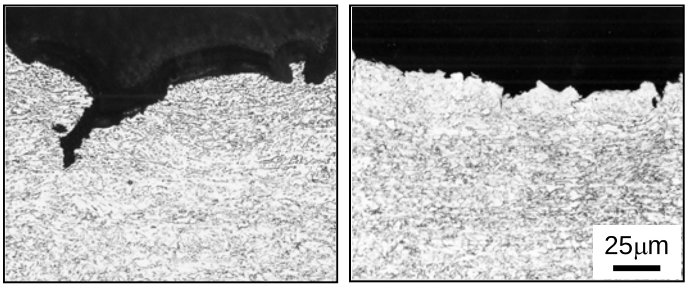


Figure 7 SEM micrographs of notch root surface of Pipe C (X80) specimen after the SCC test.

After the SEM observation of the notch root surface, the specimen was cut in the center of the specimen, and cross section was observed. Figure 8 shows the example of optical microscope observation of Pipe A specimen in the 0.3mm depth notch. In the SEM observation, cracking was found in both polished and mill scale side. In Figure 8, about 30μm depth crack was found in the polished side, but very narrow cracks were observed in the mill scale side. It is clearly the better way to determine the crack initiation in the notch region by SEM observation of notch root surface than crass section observation only in the one section from 10mm width of the specimen. Therefore, susceptibility to SCC was determined by the SEM observation in this SCC test.

All the results of near neutral pH SCC test under cyclic loading with the cathodic potential of –1000mV were summarized in Table 5. X80 linepipes were tested in the different testing firm. Susceptibility to SCC was ranked by the marks of "C", "CC" or "CCC", as explained in Table 5. Results of Pipe A by testing firm 1 was less susceptible than other firms, but all other data exhibit almost the same results. All three kinds X80 linepipes manufactured in three different pipe manufacturer showed the same susceptibility to near neutral pH SCC as conventional grade of X65 linepipe.



(a) Polished side (b) Mill scale side

Figure 8 Cross section of Pipe A (X80) specimen in 0.3mm notches.

Table 5 Results of the near neutral SCC test.

No	Grade	side	Testing firm		
			1	2	3
A	X80	polished	**CC**	**CC**	**CC**
		mill scale	**C**	**CCC**	**CCC**
B	X80	polished	**-**	**CC**	**-**
		mill scale	**-**	**CC**	**-**
C	X80	polished	**-**	**-**	**CC**
		mill scale	**-**	**-**	**CCC**
D	X65	polished	**-**	**CC**	**-**
		mill scale	**-**	**CCC**	**-**

Susceptibility

High ↑ CCC : Crack at 0.1 to 0.3mm depth notches
CC : Crack at 0.2 and 0.3mm depth notches
C : Crack at 0.3mm depth notches only
Low NC : No crack

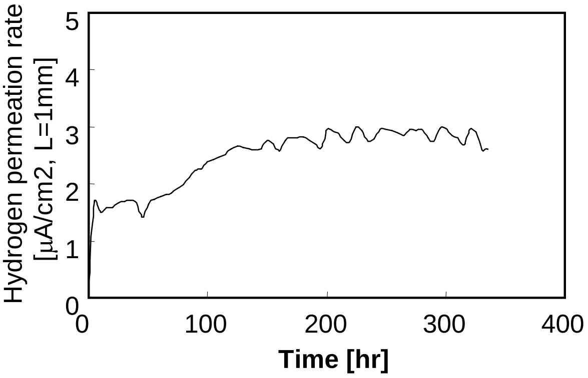
4. DISCUSSIONS

4.1 Hydrogen permeation

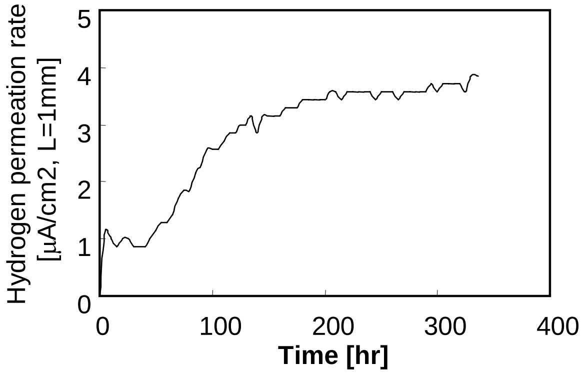
Hydrogen permeation test was conducted to investigate the effect of hydrogen in the SCC test. Pipe A (X80) and D (X65) were used, and hydrogen permeation by the NS4 solution with cathodic charge of –1000mV vs. SCE was measured. Hydrogen permeation rate, hydrogen permeation current divided by area of the specimen connected to the solution, for both pipes was shown in Figure 9. There was not a large difference in the saturated hydrogen permeation rate for both steels. Hydrogen content by hydrogen permeation was given by following equation [20];

$$C_0(\mathrm{ppm}) = J_\infty(\mathrm{A/cm^2})\ L(\mathrm{cm})/D(\mathrm{cm^2/s}) \times 1.318 \qquad (1)$$

where, C_0 , J_∞, L and D are hydrogen content, saturated hydrogen permeation rate, thickness of the specimen and diffusion coefficient, respectively. Given the hydrogen diffusion rate as $D=5\times10^{-5}$ cm^2/s for X80 linepipe steel, hydrogen content was calculated as about 0.1ppm. This hydrogen content seems to be a small value, however it should be enough for cause hydrogen embrittlement. Furthermore, this data was obtained in the flat specimen, and hydrogen content should be higher in the stress concentration region, resulting in strong influence of hydrogen embrittlement.



(a) Pipe A (X80)



(b) Pipe D (X65)

Figure 9 Hydrogen permeation rate of Pipes A and D under NS4 solution with cathodic polarization.

4.2 Effect of rolling direction on SCC

SCC is considered to occur in the stress field caused by fluctuation of service pressure, i.e. hoop stress plays a significant role, and cracks usually extend in the longitudinal direction. In the UOE linepipe, crack extension should be parallel to the rolling direction of the steel plate. However, in the SCC test proposed in this work uses longitudinal specimen with the notches introduced in circumferential direction, not in the rolling direction. Therefore, the effect of rolling direction on SCC testing should be clarified.

Steel plate for Pipe C was used for the SCC test and specimens were taken in the both longitudinal direction, same as rolling direction, and transverse direction. Then, cyclic loading test in the NS4 solution with cathodic charge of –1000mV vs. SCE was conducted, exactly the same condition as SCC test conducted on the pipe specimens. In order to simulate the strain induced by pipe forming process, 1.8% pre-strained sample was also prepared in the transverse direction.

Test results were summarized in Table 6. Specimen in the transverse direction was less susceptible to cracking. However, by comparing to the SCC test data of X80 and X65 linepipes, as shown in Table 5, it should be considered that the effect of rolling direction was not so significant.

Table 6 Results of the near neutral SCC test on the X80 plate.

No	Grade	Direction	Straining	Side	Result
C	X80	Longi.	None	polished	**CCC**
				mill scale	**CCC**
		Trans	None	polished	**CC**
				mill scale	**CC**
			1.8%	polished	**CCC**
				mill scale	**CCC**

4.3 Detailed observation of the cracks

Fracture surface and cracking path were investigated using the samples after SCC test, which has relatively long crack extension. Figure 10 shows the SEM microphotograph of fracture surface of the SCC crack found in the X80 steel. Length of the SCC crack was about 25μm from the notch root. While there is a difficulty in clearly defining the fracture process, fracture surface observed in the SCC specimen can be categorized as quasi-cleavage fracture. But, the fracture surface was rougher than that is typically observed in delayed fracture caused by hydrogen embrittlement. Although, further precise investigation is necessary to clarify the mechanism of SCC, there should be some effect of corrosion or localized plastic deformation.

Crack path in the SCC specimen was investigated by SEM, as shown in Figure 11. It is clear that transgranular cracking occurred in the SCC test. Crack in the near surface region, Figure 11 (a), shows relatively wide crack opening, and shapes of both right and left side of the crack are not fit each other. This may be the evidence that corrosion plays an important role in near neutral pH SCC.

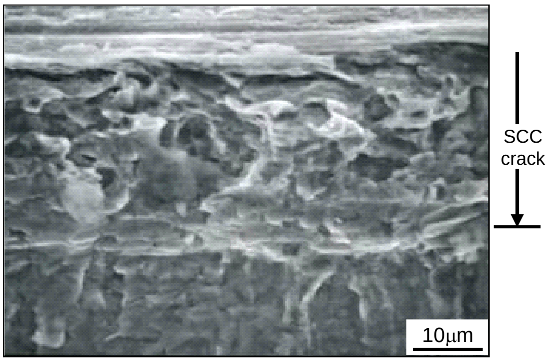


Figure 10 Fracture surface of the SCC crack found in X80 steel.

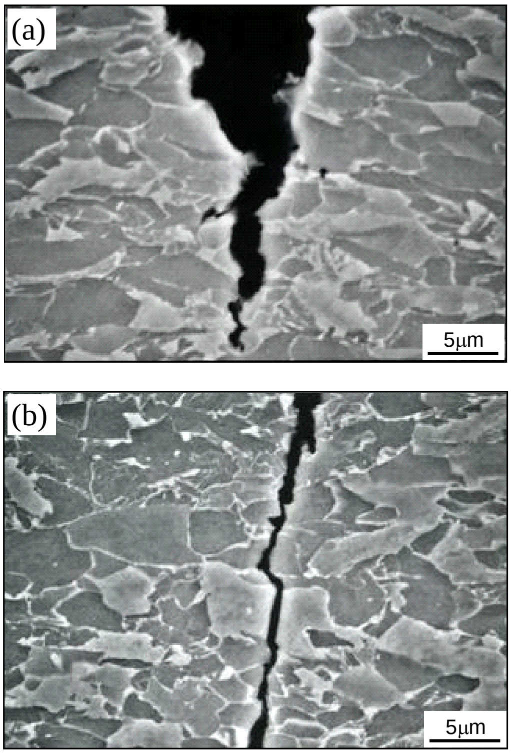


Figure 11 Cross section of SCC crack found in X80 steel

5. CONCLUSION

Susceptibility to stress corrosion cracking (SCC) of Grade X80 linepipe steels was evaluated by cyclic loading test the NS4 solution with cathodic polarization of -1000mV vs. SCE, which was the severe condition for promoting cracking. Results are summarized as follows;

(1) No significant difference in susceptibility to SCC was found between Grades X80 and X65 linepipes, both produced by TMCP process, even under higher stress condition for X80 linepipe steel.

(2) Hydrogen content of X80 steel induced by the SCC test environment, NS4 solution and cathodic charge of –1000mV, was about 0.1ppm by hydrogen permeation measurement. There should be a strong effect of hydrogen

for the cracking under the SCC test condition.

(3) There was no significant effect of rolling direction in the SCC samples on susceptibility to SCC.

(4) Transgranular cracking and quasi-cleavage fracture surface were observed as an evidence of effect of both corrosion and hydrogen embrittlement on the near neutral pH SCC.

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