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Grade X65 Linepipe with Low Surface Hardness for Severe Sour Environment

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Abstract:

Grade X65 linepipe steel plate with excellent SSC resistant properties for H_2S sour service has been developed. Optimized alloy design and controlled rolling conditions and the cooling process using Super-OLAC^{TM}-A (On-Line Accelerated Cooling) are applied to achieve a high strength and high toughness steel with uniform low surface hardness. By improving cooling uniformity as well as surface cooling rate control, homogeneous granular bainite microstructure is obtained, resulting in stable low surface hardness. UOE pipes using the developed steel plates achieved superior SSC resistant properties in the small scale four-point bend (4PB) test and full ring test even in 16bar H_2S high pressure conditions.

1. Introduction

API X65 (YS450 N/mm^2) high strength linepipe is widely used for pipeline transportation of natural gas containing hydrogen sulfide (H_2S). In addition to strength and toughness, sufficient resistance against hydrogen induced cracking (HIC) and sulfide stress corrosion cracking (SSC) is also required in these sour service environments. Therefore, in the steel plates used in high strength X65 sour resistant linepipe, inclusions and segregation must be reduced as far as possible, as these material defects form points of origin of HIC, and it is also necessary to achieve high strength, toughness and HIC resistance performance simultaneously by obtaining a homogenous fine bainite microstructure[1, 2]. However, it has been reported that SSC susceptibility increases as the hardness of steel materials increases [3, 4], and for this reason, the upper limit value of hardness is regulated for the linepipe used in sour environments [5]. Recently, linepipe has been used in severe sour environments with a H_2S partial pressure exceeding the 1 bar of the conventional standard for severe sour service and high-pressure operation of pipelines. After an accident due to SSC in a sour gas pipeline using linepipes manufactured in the 2000s, reevaluation of the SSC resistance performance of linepipes using steel plates manufactured by the controlled rolling and controlled cooling process (thermomechanical control process: TMCP) has received much attention [6–8].

Since the 1980s, high cooling rates were achieved by the development of the accelerated cooling process after rolling, and it became possible to obtain high strength and high toughness even in heavy thickness steel plates [10–12]. On the other hand, higher cooling rates increase surface hardness, resulting in the problem of an increased danger of SSC. The influence of hardness on the behavior of SSC has mainly been investigated in quenched and tempered oil well products (oil country tubular goods: OCTG), which have relatively high strength, and in welds, which may increase local hardness [13, 14]. Although the strength of the steel plates used in sour resistant linepipe is lower than that of OCTG products, surface hardness is sometimes increased by general accelerated cooling, and the relationship with SSC has been discussed [6, 7]. In order to minimize the risk of SSC in recent severe sour environments, high-precision cooling control technology is required in order to suppress excessive surface harden-

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ing and ensure a uniform surface hardness distribution in the whole steel plate.

In 2011, JFE Steel's West Japan Works installed the *Super*-OLAC™-A, a controlled cooling technology that enables high-precision control of cooling uniformity and the cooling rate, and applied this advanced technology to a wide variety of high-performance steel plates, including plates for linepipes [12]. Use of the *Super*-OLAC-A makes it possible to obtain a surface layer composed mainly of soft granular bainite and stably reduce the hardness of the surface layer over the entire surface of the steel plate. This paper introduces the material design concept for achieving SSC resistance performance suitable for severe sour environments in which the H_2S partial pressure exceeds the 1 bar of the conventional standard. Grade X65 sour resistant linepipe with excellent SSC resistance performance even in high-pressure H_2S environments was developed, and its SSC resistance performance is mainly reported.

2. Material Design Concepts for Achieving SSC Resistance Performance

2.1 Material Design Concepts

In the design of sour resistant linepipe, a material hardness limit is applied in order to avoid SSC, as shown in the NACE MR0175/ISO 15156 -1 standard, and a hardness upper limit of 22 HRC (approx. 250 HV10) is set for carbon steel and low alloy steel [5]. In API Spec 5L, which is a standard for general linepipe, the hardness limit is regulated to 250 HV10 or less at a position 1.5 mm from the surface of the pipe inside and outside surfaces. These hardness specifications are applied to many sour resistant linepipes, and safety for SSC has been verified in the conventional test in a H_2S environment of 1 bar or less. However, SSC tests in severe H_2S environments over 1 bar have seldom been carried out, and there are many unclear points concerning the suitability of materials. On the other hand, following a recent pipeline accident caused by SSC, the focus has been on the formation of the 'hard-spot' area at the extreme surface region of linepipe materials produced by TMCP. Since it is difficult to measure the cross-sectional hardness of the surface layer at a position only 0.25 to 0.5 mm near the surface side due to the large size of the indentation under the conventional test load of 10 kg, a method of measurement at a low load of 0.1 kg or 0.5 kg has been proposed. Here, the relationship with SSC resistance performance in H_2S environments over 1 bar was investigated from the viewpoints of the microstructure and hardness of the extreme surface layer of the pipe.

Figure 1 shows a schematic illustration of the temperature history of the center of thickness position and the surface position during accelerated cooling. In general, accelerated cooling is a process in which a steel plate is cooled with water from the plate surface, and the cooling rate of the surface layer is faster than that of the center of thickness. Therefore, it is important to control the cooling rate of the surface layer in order to lower surface hardness. **Figure 2** shows the relationship between the surface cooling rate and the microstructure of a X65 linepipe steel in a CCT schematic diagram. At high cooling rates exceeding 200°C/s, the microstructure consists mainly of hard lath bainite (LB), while at low cooling rates below 50°C/s, it consists mainly of soft granular bainite (GB). **Figure 3** shows typical microstructures of the LB structure and GB structure at a depth of 0.25 mm. **Figure 4** shows the relationship between the cooling rate of the surface layer and the maximum hardness HV0.1. The Vickers hardness was measured, but under a normal load of 10 kg, the dent

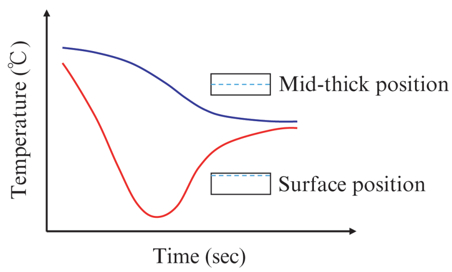


Fig. 1 Schematic illustration of cooling curve in steel plate

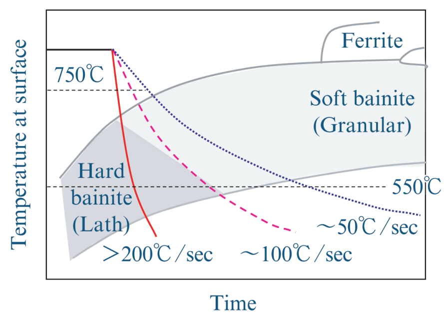


Fig. 2 Schematic illustration of CCT diagram of X65 sour linepipe steel

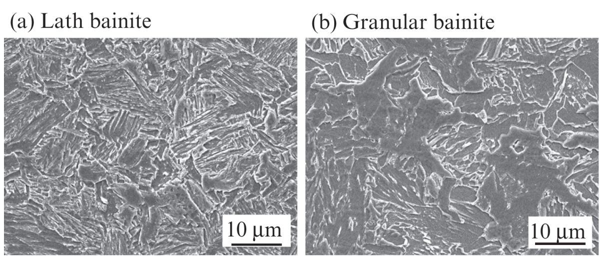


Fig. 3 Typical surface microstructure of (a) lath bainite and (b) granular bainite

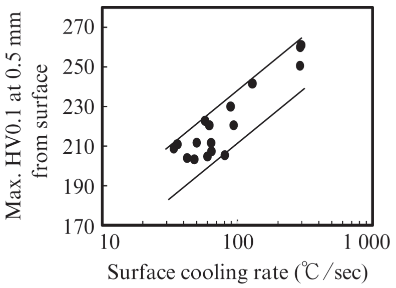


Fig. 4 Relationship between surface cooling rate and maximum surface hardness in grade X65 steel plate

size was large and measurement of the extreme surface layer was difficult, so a load of 0.1 kg was adopted. It was found that surface hardness decreased as the cooling rate decreased.

2.2 Relationship between Cooling Rate and Surface Microstructure and Hardness

Detailed microstructural observations were carried out for pipes manufactured using steel plates with different cooling rates. **Figure 5** shows the effect of the cooling rate on the surface microstructure. In the steel for X65 linepipe, the surface microstructure usually forms a bainite structure. The bainite structure is generally based on bainitic ferrite (BF) formed in a lath, and bainite is often classified into upper bainite in case of carbide precipitation at the BF interface or no precipitation, and lower bainite in case of carbide precipitation in the BF grains [15]. However, in low carbon steels such as linepipe steels, BF grows into grains (granular) when the cooling rate is slow, and is classified into lath bainite (LB) and granular bainite (GB) according to the morphology of the BF. LB is predominant when the cooling rate is over 200°C/s and has a high hardness over 300 HV, but when the cooling rate

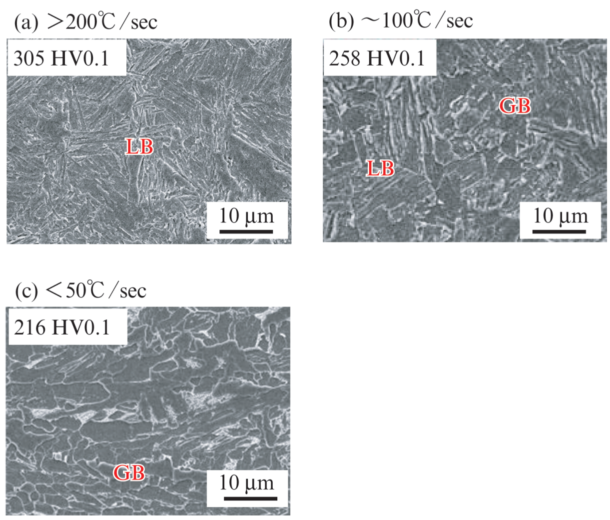


Fig. 5 Effect of surface cooling rate on surface microstructure

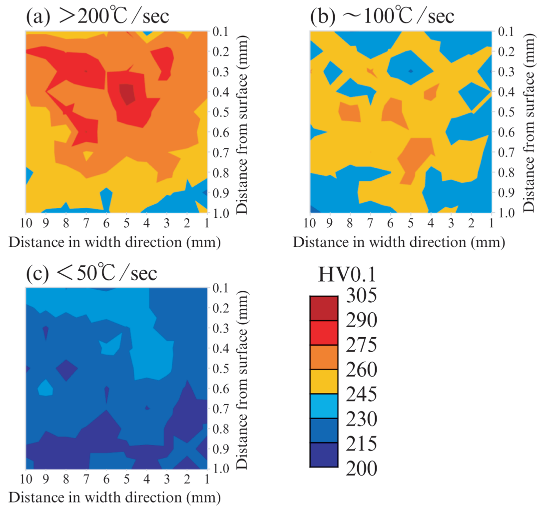


Fig. 6 Surface hardness distribution in three different cooling rates of steel pipe

is approximately 100°C/s, the microstructure becomes a mixture of GB in LB, and the hardness decreases. When the cooling rate is lower than 50°C/s, GB is predominant and the hardness decreases further. **Figure 6** shows an example of the hardness distribution of pipes manufactured using three types of steel plates with different cooling rates. The pipes made of steel plates with high cooling rates of more than 100°C/s tended to have high hardness in both the thickness and width directions, but in contrast, the hardness was low over a wide region in both the thickness and width directions when the cooling rate was less than 50°C/s. Especially at this low cooling rate, the hardness at the position 0.25 mm from the surface is stably lower than 250 HV0.1. Using these pipes, four-point bend SSC tests and actual full ring pipe SSC tests were carried out.

3. SSC Resistance Performance of X65 Linepipe

3.1 Four-Point Bend SSC test

3.1.1 Experimental method

In order to evaluate SSC resistance performance, four-point bend SSC tests were conducted under various H_2S partial pressure conditions in accordance with NACE TM0316 standard [16]. The test materials were X65 linepipes with a thickness of 20 mm and 30 mm and outer diameter of from 711.2 mm to 914.4 mm produced by the UOE process using steel plates with the 3 different surface cooling rates shown in the previous section. The four-point bend test pieces were taken from the inside surface of the pipes after aging treatment at 250°C for 1 h, corresponding to the thermal history in outer surface coating. The SSC test conditions are shown in **Table 1**. In the test using the NACE TM0177A solution [17], the partial pressure of H_2S was

Table 1 Four-point bend test conditions

Test solution (NACE TM0177)	pH (Ini. /Fin.)	Partial pressure (bar)		Duration (hr)
		H_2S	CO_2	
Solution A (5.0 wt%NaCl + 0.5 wt%CH3COOH)	2.6 to 2.8 /4.0	1	–	720
		8	5	
		16	5	
Solution B (5.0 wt%NaCl + 2.5 wt%CH3COOH + 0.41 wt%CH3COONa)	3.4 to 3.6 /4.0	0.07	0.93	720
		0.1	0.9	
		0.13	0.87	

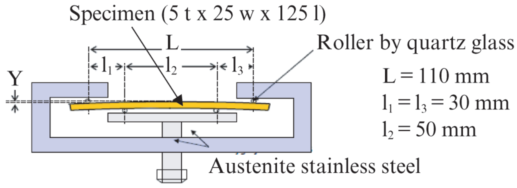


Fig. 7 Schematic illustration of four-point bend loading jig

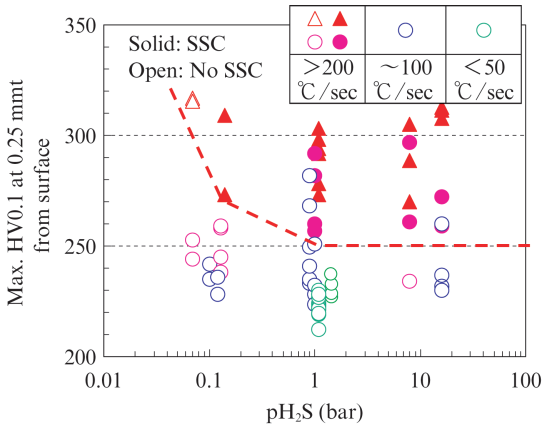


Fig. 8 Effect of H_2S partial pressure and surface hardness on SSC by four-point bend test

in the range of 1 to 16 bar. Under the conditions of H_2S partial pressures of 8 bar and 16 bar, a gas mixture with 5 bar CO_2 was used. In the test using the NACE TM0177B solution [17], the partial pressure of H_2S was in the range of 0.07 to 0.13 bar and the total gas pressure was adjusted to 1 bar by mixing CO_2. **Figure 7** shows a schematic diagram of the jig for the four-point bend SSC test. The pipe inner surface was set to the tensile side of four-point bend, and the applied stress was 90% of the actual YS. The test time was 720 h. After the test, the central part of the test piece was cut and polished, and the existence of cracking was evaluated. Using the same cut test piece, the hardness HV0.1 at the position 0.25 mm from the surface was measured, and was evaluated at the maximum value of 20 measurement points.

3.1.2 Experimental Results and Discussion

Figure 8 shows the results of the four-point bend SSC test. The figure shows the maximum value of the surface hardness of each test piece, the H_2S partial pressure (pH_2S) and the condition of SSC cracking. In the case of H_2S partial pressures over 1 bar, the limit of surface hardness without cracking in the four-point bend SSC test was about 250 HV0.1. At 0.13 bar, the limit of surface hardness was about 270 HV0.1, and SSC was not observed at 0.07 bar. SSC was observed only in samples with high cooling rates exceeding 200˚C/s. As mentioned in the previous chapter, samples with a high cooling rate of more than 200˚C/s displayed high hardness exceeding 250 HV0.1 over a wide range in the thickness direction (about 1 mm) and width direction (about 10 mm). Therefore, it is considered that the crack tends to propagate in the thickness direction when SSC occurs.

As a result of the experiment, it became clear that the surface hardness of the pipe inside surface rose when volume fraction of the LB structure increased under the H_2S partial pressure over 1 bar, and SSC occurred easily under this condition. It was also proven that high SSC resistance performance can be obtained under H_2S partial pressure conditions over 1 bar by reducing the hardness at the surface layer 0.25 mm position to 250 HV 0.1 or less by suppressing the LB structure and obtaining GB the main structure.

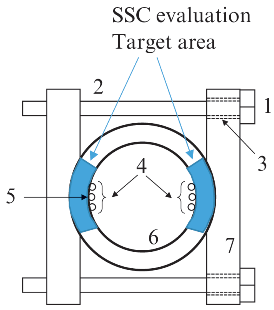
3.2 Full Ring SSC Test

3.2.1 Experimental method

Full ring SSC tests were carried out in order to evaluate SSC resistance performance and to investigate the correlation with the four-point bend test. As in the four-point bend SSC test, the test samples were X65 linepipes with a thickness of 30 mm and outer diameter of 711.2 mm and different surface hardnesses. The H_2S partial pressures were 1 bar and 16 bar, and the test was carried out based on BS 8701 standard [18]. The test solution and H_2S partial pressure conditions for the full ring SSC test are shown in **Table 2**. In the test using the NACE TM0177A solution and the H_2S partial pressure of 16 bar, a mixed gas with 5 bar CO_2 was used. **Figure 9** shows a schematic illustration of the stress loading method in an full ring SSC test. The samples were aged at 250°C for 1 h, and the surface scale was removed by shot blasting. **Table 3** shows the surface cooling rate, the surface hardness of the pipe inner surface and the applied stress conditions for the test. The applied stress was measured by a strain gauge attached to the inner surface of the test pipe, and a condition from 72% of the standard lower limit yield stress to the stress equivalent to 80% of the actual yield

Table 2 Test solution and H_2S pressure condition

Test solution (NACE TM0177)	pH (Ini. /Fin.)	Partial pressure (bar)		Duration (hr)
		H_2S	CO_2	
Solution A (5.0 wt%NaCl + 0.5 wt%CH3COOH)	2.6 to 2.8 /4.0	1	–	720
		16	5	



1 Bolts
2 Threaded block
3 Clearance hole
4 Strain gauges
5 Location of maximum tensile strength
6 Pipe sample
7 Load distribution block

Fig. 9 Schematic illustration of full ring SSC test

Table 3 Full ring SSC test matrix

Steel	Cooling rate at surface (˚C/sec)	HV0.1 max. at 0.25 mmt	Applied stress (MPa)	
			1 bar H_2S	16 bar H_2S + 5 bar CO_2
A1, A2	<50	234	360	360
B	<50	243	465	–
C	>200	293	458	–

stress was chosen.

3.2.2 Experimental results and discussion

Table 4 shows the full ring SSC test results. The table shows the maximum value of HV0.1 at the 0.25 mm position in the pipe inner surface of each sample and the SSC test results under the two H_2S partial pressure conditions. In pipes A1 and A2 with low surface hardness, no SSC was observed under both conditions of 1 bar and 16 bar. **Figure 10** shows the appearance of the pipe inner surface after the test of pipe A1, and **Fig. 11** shows the microstructure of the surface layer in the longitudinal center of the pipe. Under the high pressure condition of 16 bar, the amount of corrosion tended to be slightly large, but SSC did not occur. As shown in **Fig. 12**, SSC was not observed at the H_2S partial pressure of 1 bar even under the condition of high applied stress in pipe B with low surface hardness, but in pipe C with the surface hardness exceeding 250 HV0.1, SSC occurred under the same applied stress condition as in pipe B, as shown in **Fig. 13**. This result is in good agreement with

Table 4 Full ring SSC test results

Steel	Cooling rate at surface (˚C/sec)	HV0.1 max. at 0.25 mmt	Test result	
			1 bar H_2S	16 bar H_2S + 5 bar CO_2
A1, A2	<50	234	No SSC	No SSC
B	<50	243	No SSC	–
C	>200	293	SSC	–

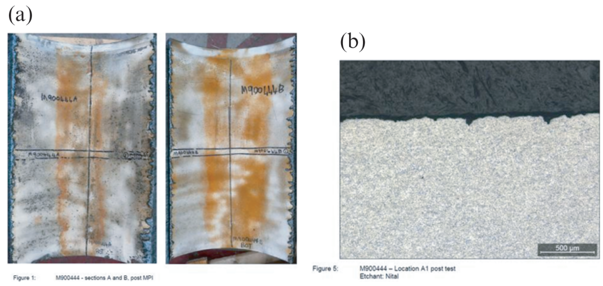


Fig. 10 Test pipe A1 after full ring SSC test at 1 bar H_2S((a) Pipe inner surface of target area (b) Micrograph of pipe inner surface)

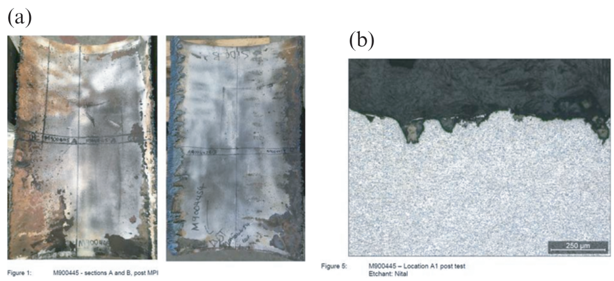


Fig. 11 Test pipe A2 after full ring SSC test at 16 bar H_2S ((a) Pipe inner surface of target area (b) Micrograph of pipe inner surface)

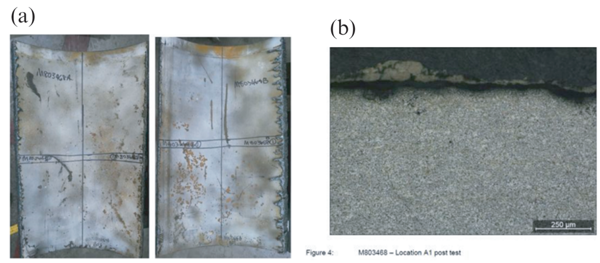


Fig. 12 Test pipe B after full ring SSC test at 1 bar H_2S ((a) Pipe inner surface of target area (b) Micrograph of pipe inner surface)

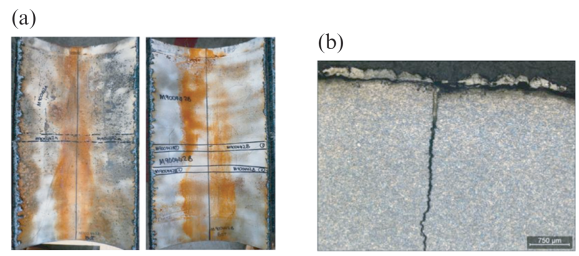


Fig. 13 Test pipe C after full ring SSC test at 1 bar H_2S ((a) Pipe inner surface of target area (b) Micrograph of pipe inner surface)

Table 5 Mechanical properties of developed UOE pipes

Steel	Thickness (mm)	OD (mm)	AsUOE Aged	Tensile properties*			Charpy			DWTT**
				YS (MPa)	TS (MPa)	EL (%)	vE (J) at −30°C			SA (%) at −10°C
							BM	WM	HAZ	
Developed	30	711.2	AsUOE	519	593	56	476	197	132	100
			Aged	531	625	54	470	193	485	–
Specification of IOGP (tentative)				≥ 450	≥ 535	≥ 24	≥ 40			≥ 85

Steel	Thickness (mm)	OD (mm)	AsUOE Aged***	HV0.1 max. at 0.25 mm			4PB SSC Test
				BM	WM	HAZ	
Developed	30	711.2	AsUOE	217	241	231	No SSC
			Aged	237	237	242	
Specification of IOGP (tentative)				≤ 245			No SSC

* API rectangular specimen, transverse direction
** 19 mm reduced thickness specimen
*** Simulated coating heat treatment (250°C ×1 hr)

the result of the four-point bend SSC test in Fig. 8 in the previous section. From the above, it was proven that lowering the surface hardness was effective for preventing SSC in the full ring SSC test, including the high pressure H_2S condition of 16 bar.

4. Mechanical Properties of Developed Grade X65 Linepipe with Low Surface Hardness for Severe Sour Environments

Table 5 shows the mechanical properties of the developed X65 linepipe. The characteristics of the heat-treated pipe corresponding to the thermal history due to outer coating are also shown. The developed X65 linepipe has high strength and excellent base metal toughness and welded joint toughness in spite of its heavy wall thickness of 30 mm, and the hardness of the pipe inner surface also showed a stable low value. These characteristics satisfy the draft international standard (IOGP S-616) for pipelines.

5. Conclusion

This report presented the material design concept of a newly-developed grade X65 linepipe with low surface hardness for severe sour environments. The features of the developed steel and the results obtained are summarized as follows. It is considered that the application of the developed linepipe can contribute to further improvement of the safety of pipelines for sour gas transportation.

(1) As a result of an examination of pipes using steel plates manufactured in a mill under various cooling conditions, the inner surface hardness of the pipes increased with an increase in the volume fraction of the LB microstructure.

(2) The four-point bend SSC test revealed that the hardness threshold of the pipe inner surface in each H_2S partial pressures condition. Control of SSC cracks became possible by lowering the surface hardness by suppressing the LB microstructure and achieving mainly a GB microstructure.

(3) Full ring SSC tests demonstrated that lowering surface hardness was effective for preventing SSC under both 1 bar and 16 bar high pressure H_2S conditions. The results of the full ring SSC test were also in good agreement with the results of the four-point bend test.

(4) In order to achieve high SSC resistance performance in the X65 linepipe, it was found that lowering the surface hardness HV0.1 at the surface 0.25 mm position to 250 or less is effective.

(5) The developed X65 linepipe has high strength and excellent base metal toughness and welded joint toughness in spite of its heavy wall thickness of 30 mm, and the hardness of the pipe inner surface also showed a stable low value.

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