CORROSION SCIENCE AND TECHNOLOGY, Vol.7, No.5(2008), pp.288~295

High Strength Low Alloy Steel for Sour Service

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The increase use of natural gas as an energy source has been continuous demand for ever-increasing strength in gas transmission pipeline materials in order to achieve safe and economic transportation of natural gas. In particular, linepipe material for sour gas service primarily needs to have crack resistant property. However, applications of sour linepipes are expanding toward deep water or cold region, which require higher toughness and/or heavier wall thickness as well as higher strength. To improve the crack resistance of linepipe steel in sour environment, low alloy steel are produced by controlled rolling subsequently followed by the accelerated cooling process. This paper summarizes the design concepts for controlling crack resistant property low alloy linepipe steels for sour gas service.

Keywords *: sour service, hydrogen induced cracking, linepipe steel*

1. Introduction

The need for higher strength steels for sour environments have become more apparent with the increasing energy demands and the decrease of easily obtained non-sour reserves. Many metallurgical factors influence the HIC resistance. These factors include the strength level of the steel, its microstructure, and the composition of the steel.

HIC in steels is due to ingression of hydrogen atoms into microstructural discontinuities such as inclusions, grain boundaries and hard second phases. HIC proceeds parallel to rolling direction even without externally applied stress. Metallurgical factors relating to cracking indicate that large inclusion such as elongated MnS and clusters of oxide decrease the resistance to HIC. HIC propagates along the band structure of ferrite and perarlite in hot rolled low carbon steel.1) In addition, formation of hard phases such as M/A constituents and bainite also increases HIC susceptibility of steels according to their fraction in steel matrix.2),3) The fundamental requirements for linepipe steels intended for sour service can be defined in terms of the cleanness and the toughness of the material. As the requirements for mechanical properties and HIC resistance of materials for sour service, the manufacturing processes for sour material have to be optimized to meet the requirements. With a view of steelmaking process, a production of a clean slab with minimized amounts of non-metallic inclusions and a sound slab which implies reduced center-line segregation was the most important technique to produce linepipe steel for sour service. To meet the requirements for mechanical properties as well as HIC resistance the steel composition and the process parameters for plate rolling have to be designed properly. Recently, Thermo-Mechanical-Control Process (TMCP) is employed to produce the linepipe steel plate. TMCP utilizes the different metallurgical mechanisms and provides a large number of microstructures to achieve various objectives. The required mechanical properties in combination with HIC resistance can be obtained by controlling the parameters of TMCP.

As the strength level and the thickness of plate for sour service was increased, the composition of steel have to be varied to meet the requirements. Among the various alloying elements, Cr and Mo usually are added High Strength Low Alloy (HSLA) steel because this addition has tremendous effects on microstructure. So, In this study, the effect of Mo addition with combined TMCP parameters on HIC resistance and mechanical properties was discussed.

2. Experimental procedures

Materials used in this study were X65 grade linepipe steels for sour service and laboratory vacuum melt steels. The chemical composition of the steel plate is listed in Table 1. All tested steels belong to API X65 grade according to API5L specification.4)

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Table 1. **Chemical composition of the experimental steel (wt. %)**

	C	Mn	Si	P	S	Nb + Ti + V	Cu + Ni + Cr	Mo
A	< 0.05	1.2	0.25	< 0.01	< 0.002	> 0.15	> 0.5	0
B	< 0.05	1.2	0.25	< 0.01	< 0.002	> 0.15	> 0.5	0.17
C	< 0.05	1.2	0.25	< 0.01	< 0.002	> 0.15	> 0.5	0.27

In order to observe the effect of Mo addition on the properties of tested steels, the content of Mo was changed at a three level such kind of 0, 0.17, and 0.27 wt%. The ingots were heated and hot-rolled to 20 mm thick and finally were cooled by accelerated cooling process. In order to observe the effect of TMCP parameters on the properties of same composition steels, the start cooling temperature (SCT) and finish cooling temperature (FCT) at three different levels. Fig. 1 shows the accelerated cooling procedures and the notation of obtained specimens.

For observation of the steel microstructure, the specimens were then degreased with acetone and chemically etched with a 5% nital solution (a mixture of 5 ml nitric acid and 95 ml ethanol). The microstructure was observed using the optical microscope (OM) and the scanning electron microscope (SEM). For determination the characteristics of the uncertain phases in the test steel, the Ultra-micro Vicker`s hardness testing was performed with denting load of 10gf. The yield strengths and tensile strengths were evaluated in reference to ASTM E8-93 Method (Standard Test Methods for Tension Testing of Metallic Materials).

The HIC resistances of test steel were obtained in reference to NACE TM0284-2003 method.[5] The test solution consists of 5.0 wt% NaCl and 0.5 wt% glacial acetic acid dissolved in distilled water. Solution was deaerated by bubbling N_2 gas into the solution for a minimum period of 1 h/L of test solution and then saturated with H_2S gas (1atm partial pressure). The pH value of test solution was about 2.9 and the temperature of test solution was maintained to room temperature during testing. The HIC standard specimen with 100 mm long by 20 mm wide had the full thickness of the steel plate. All HIC specimens were taken from the steel plate with the longitudinal axis of the steel plate. Prior to testing, the test specimens were ground up using abrasive paper to eliminate the surface scale and then rinsed with acetone. After rinsing, test specimens were stored in a desiccator. For deaeration of testing condition, N_2 gas continuously flowed into a desiccator and the prepared test solution were poured into a desiccator. After exposure during 96 hours, each test specimen was cleaned to remove scale and deposits. In order to determine the crack morphology and position, ultrasonic detection testing was performed. HIC resistance was evaluated in terms of crack length ratio (CLR) and crack area ratio (CAR). After HIC testing, fracturing behavior was investigated by optical microscopy (OM), scanning electron microscopy and energy disperse spectroscopy (EDS)

3. Results and discussion

3.1 Effect of Mo addition on the microstructure

It has known that the addition of Mo can increase the A_3 temperature and decrease the B_s and M_s temperatures and delay the transformation of ferrite and pearlite.[6] In

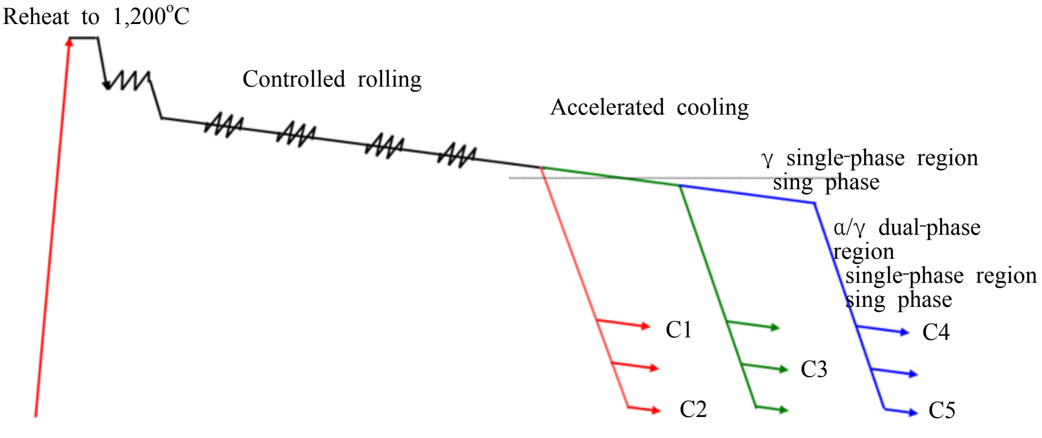
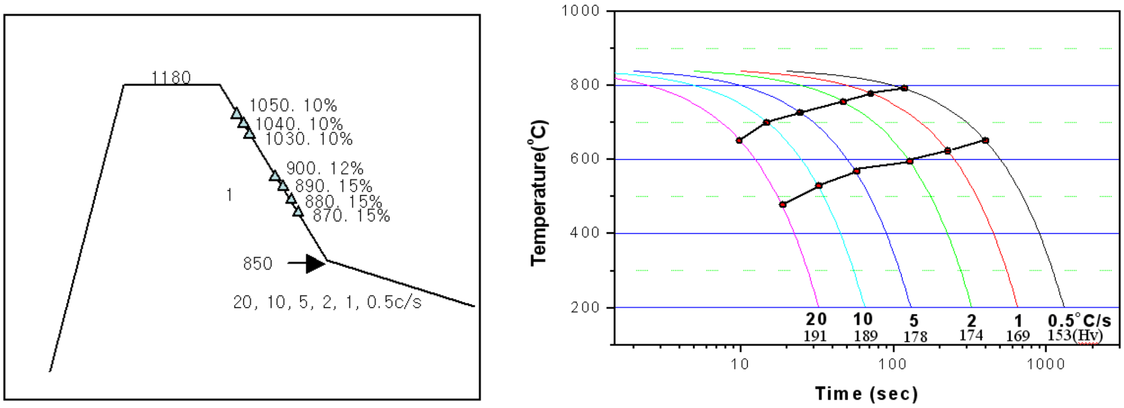


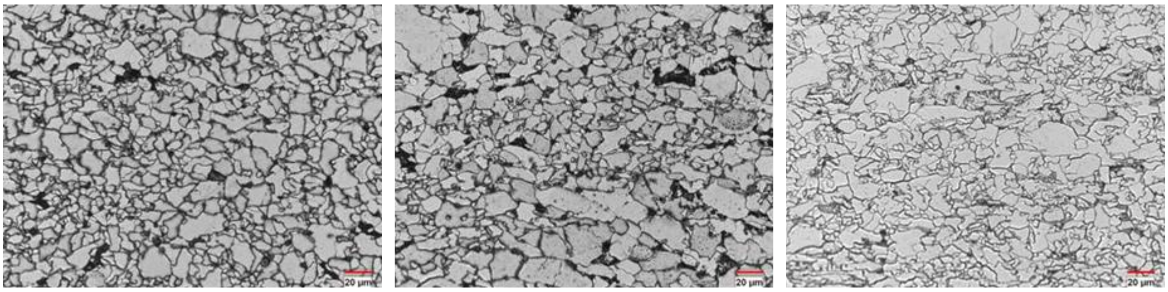
Fig. 1. Schematic of the accelerated cooling process to produce difference microstructures.

order to observe the effect of Mo on the phase transformation and the microstructure, dilatometric tests were carried out and the microstructures were observed after dilatometric tests. Fig. 1 shows the test condition of dilatometric test and the deformed CCT curve of specimen A (without Mo). The start and end temperature of phase transformation can be determined through the dilatometic test, as shown in Fig. 2. The start temperature of ferrite transformation is depend on the cooling rate. In air cooling case, the start temperature (Ar_3 temperature) is about 800℃. The microstructure of each specimen after dilatometric test is shown in Fig. 3. The change of microstructure with cooling rate is obviously shown in Fig. 3. At lower cooling rate below 10℃/s, the microstructure is mainly consisted of ferrite and small amount of pearlite. And the grain size of ferrite is getting smaller with increasing the cooling rate. Acicular ferrite started to be appeared at the cooling rate above 10℃/s. At the cooling rate of 20℃/s, the microstructure of specimen is a fully acicular ferrite. As shown in CCT curve, the change of hardness value with cooling rate can be explained by these changes of the microstructures.

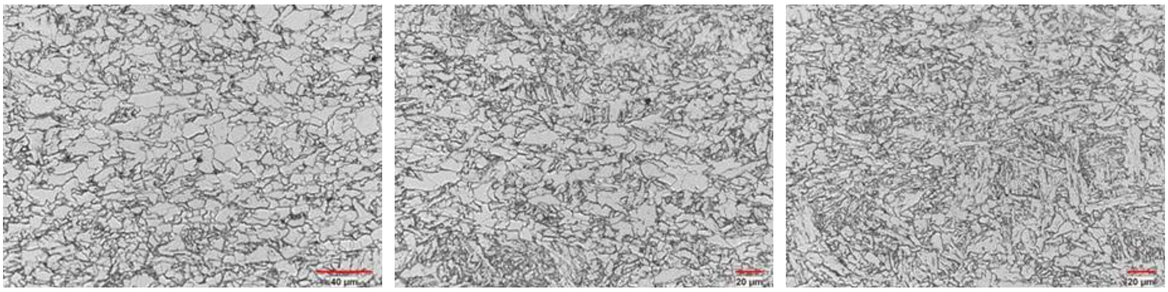


(a) (b)

Fig. 2. (a) Test conditions of dilatometric test (b) Deformed CCT curve of Specimen A



(a) 0.5℃/s (b) 1℃/s (c) 2℃/s



(d) 5℃/s (e) 10℃/s (f) 20℃/s

Fig. 3. Microstructures of Specimen A after dilatometric tests.

Mo usually is added to HSLA steels because this addition has tremendous effects on microstructure and mechanical properties. Fig. 4 shows the effect of cooling rate on the start and end temperature of transformation of specimen B (0.17 wt% Mo). Comparing to specimen A (without Mo), the start and end temperature of transformation is decreased at same cooling rate. Fig. 5 shows the microstructures of specimen B after dilatometric tests. At lower cooling rate below 2℃/s, the microstructures are consisted of ferrite and small amount of pearlite. Needless to say, the grain size of ferrite getting smaller with increasing cooling rate. At higher cooling rate of above 5℃/s, no any significant difference is observed in microstructure, fully acicular ferrite is appeared from the cooling rate of 5℃/s. From the microstructure, it is considered that the change of microstructure of specimen B is less sensitive than that of steel A to cooling rate. The fully acicular ferrite which is the best microstructure to obtain good HIC resistance can be easily formed at lower cooling rate. The change of hardness value with cooling rate shows similar trend of microstructure. No more increase is observed in hardness from the cooling rate of 5℃/s.

Fig. 6 shows the CCT curve of specimen C which have a higher Mo content (0.27 wt%). Though Mo content is increased from 0.17 wt% to 0.27 wt%, the start and end temperature of transformation is not decreased significantly.

The microstructure of specimen C at each test cooling

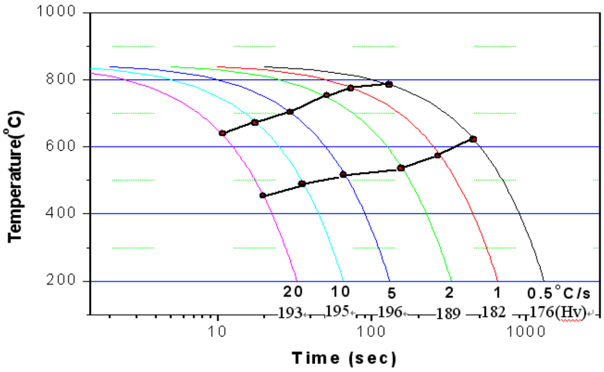


Fig. 4. Deformed CCT curve of Specimen B

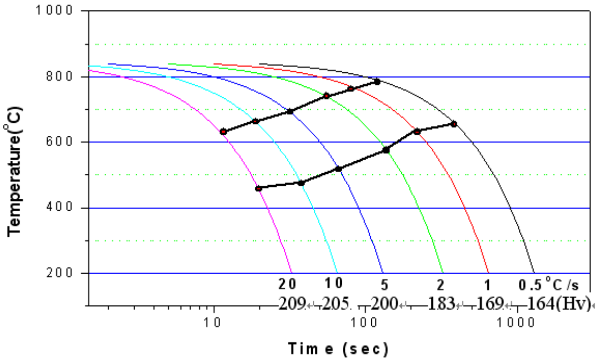
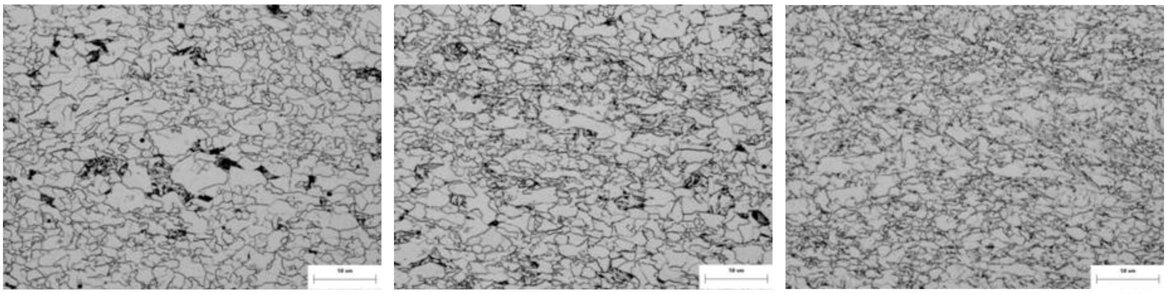
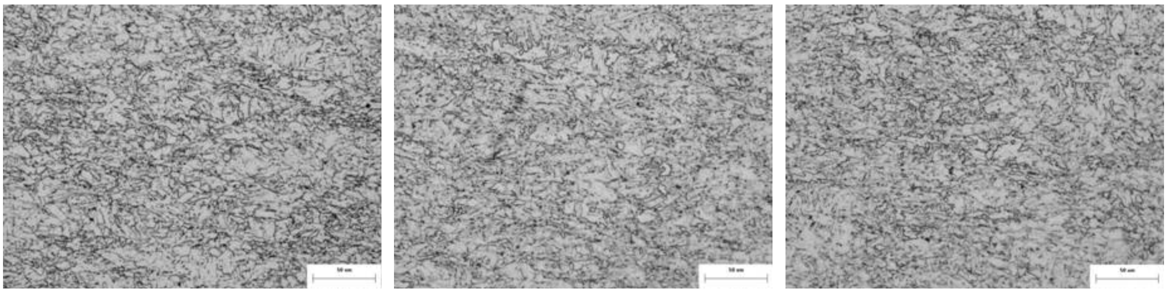


Fig. 6. Deformed CCT curve of Specimen C

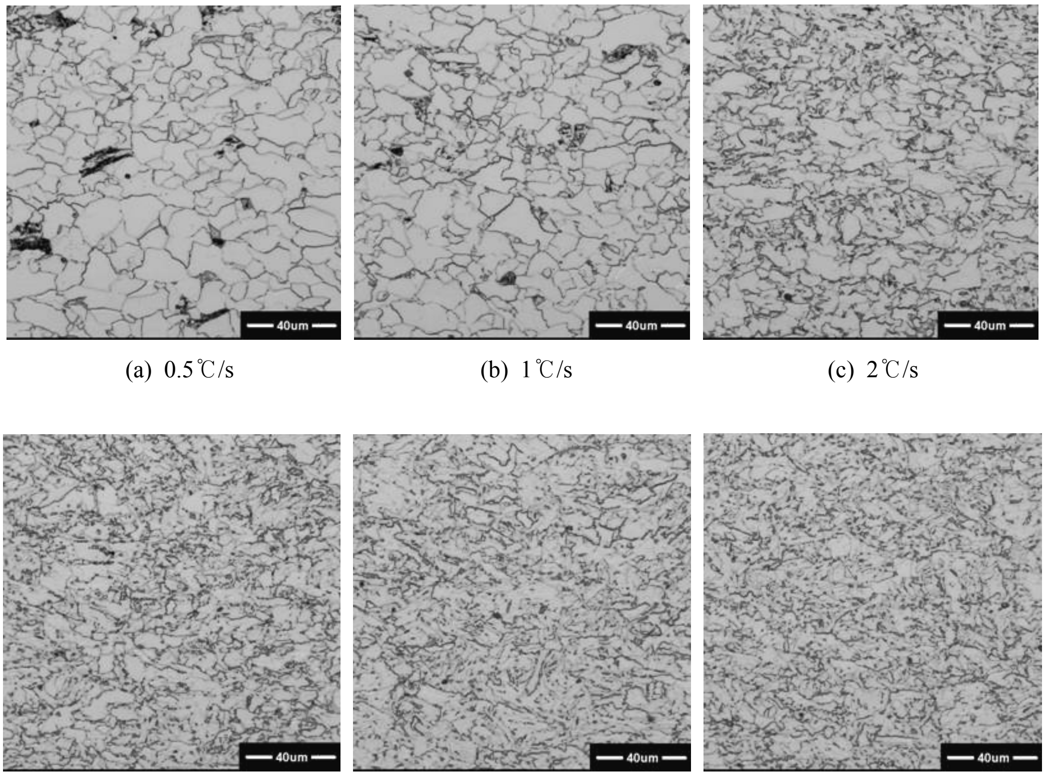


(a) 0.5℃/s (b) 1℃/s (c) 2℃/s



(d) 5℃/s (e) 10℃/s (f) 20℃/s

Fig. 5. Microstructures of Specimen B after dilatometric tests.



(a) 0.5℃/s (b) 1℃/s (c) 2℃/s

(d) 5℃/s (e) 10℃/s (f) 20℃/s

Fig. 7. Microstructures of Specimen B after dilatometric tests.

rate is similar that of specimen B at shown in Fig. 7. At lower cooling rate of below 2℃/s, ferrite and small amount of pearlite is a main phase and acicular ferrite is a main phase from the cooling rate of 2℃/s. The hardness value is increased sharply at cooling rate of 2℃/s, and acicular ferrite is started to form at this cooling rate. After fully acicular ferrite is formed, the dependency of hardness value with cooling rate is small. From the results, it is considered that the main factor is the fraction of acicular ferrite to determine the hardness value at this steel.

3.2 Effect of Mo addition on the tensile properties

The tensile properties are dependant on the alloy composition and cooling condition. In this study, tensile properties with Mo content and finish cooling temperature are evaluated as shown in Fig. 8. The yield stress is increased with increasing Mo content except one specimen. The tensile stress is also increased with increasing Mo content. The effect of finish cooling temperature on the yield and tensile strength is clear with increasing Mo content. At higher Mo content steel, the yield strength is smaller than that of lower Mo content steel. This phenomenon can be explained by the formation of low temperature transformation phase. Because of the high hardenability effect of Mo, addition of this element easily generated low temp low temperature transformation phase which is enhanced continuous yielding behavior. In this continuous yielding behavior, the yield strength is often lower than expected value.

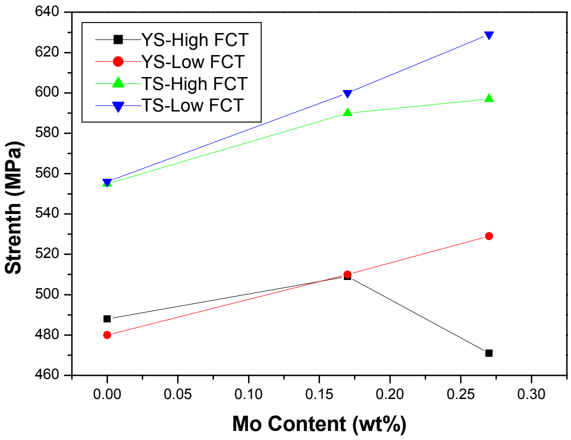


Fig. 8. Tensile properties of each specimen

Generally, the yield strength of pipe after forming is more important than that of plate because pipe properties are finally guaranteed in linepipe steel. The yield strength

Table 2. Chemical compositions and tensile properties of test specimen

No.	C	Mn	Si	P	S	Mo	Ni+Cr+Cu	Nb+Ti+V	CR [℃/s]	YS [MPa]	TS [MPa]
1	0.03	1.2	0.25	0.004	<0.002	0	<0.5	<0.15	air	423	478
2	0.03	1.2	0.25	0.004	<0.002	0	<0.5	<0.15	10	484	570
3	0.05	1.2	0.25	0.004	<0.002	0	<0.5	<0.15	air	423	488
4	0.05	1.2	0.25	0.004	<0.002	0	<0.5	<0.15	10	485	578
5	0.03	1.2	0.25	0.004	<0.002	0.3	<0.5	<0.15	air	445	571
6	0.03	1.2	0.25	0.004	<0.002	0.3	<0.5	<0.15	10	542	635
7	0.05	1.2	0.25	0.004	<0.002	0.3	<0.5	<0.15	air	406	554
8	0.05	1.2	0.25	0.004	<0.002	0.3	<0.5	<0.15	10	555	657

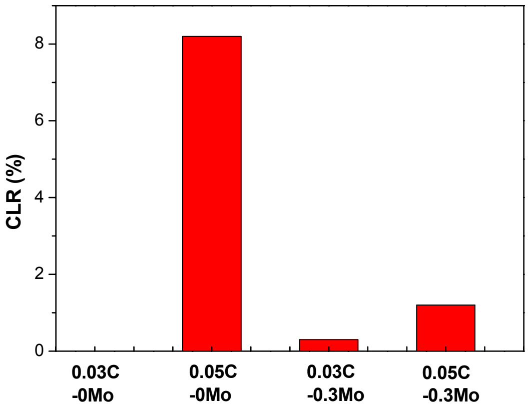
of plate is changed by strain hardening of pipe forming and baushinger effect of flattening. The amount of yield strength change from plate to pipe is dependent on the tensile behavior. In specimen A with Mo content, upper and lower yield point including yielding elongation is observed. From the tensile behavior, the decrease of yield strength is expected after pipe forming. The amount of decrement is affected by difference between higher yield point and lower yield point. In specimen B with 0.17 wt%Mo content, only lower yield point is observed. Contrary to these two specimens, continuous yielding behavior is observed in the specimen with 0.27 wt% Mo content. Therefore, the increment of yield strength is anticipated in the specimen B and C.

Consequently, although the strength depends on the cooling condition, the optimum Mo content on the X65 grade steel for sour environment at medium cooling rate is considered to be a around 0.17 wt%. At lower content, yield strength of plate can meet the specification of X65 grade steel, but yield strength of pipe might not meet the specification of X65 grade because of decrement of yield strength after pipe forming. At higher content, yield strength is very sensitive on the cooling condition. Therefore a lot of deviation is expected on the mass production line.

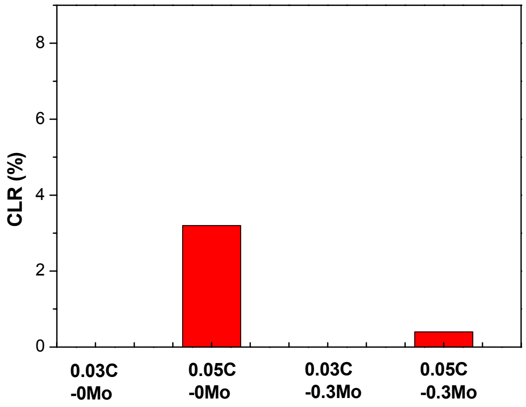
3.3 Effect of Mo addition on the HIC properties

The HIC resistance can be affected by microstructure as well as inclusion and center segregation. Especially, it is hard to get the homogeneous microstructure through thickness in the thick plate because of inhomogeneous transformation rate through thickness as well as center segregation. As mentioned in previous chapter, the addition of Mo can affect phase transformation kinetics, therefore microstructure can be changed at the same cooling condition. Therefore, microstructure homogeneity can be improved by the addition of Mo. This improvement of microstructure homogeneity resulted in the positive effect on the HIC resistance. In this study, the effect of Mo on the HIC resistance was investigated. Table 2 shows the chemical compositions and tensile properties of test specimen.

The HIC resistance can be affected by the strength of specimen. Tested samples were separated into the two groups such kind of lower grade steel (No. 1, 3, 5, 7)



(a) Lower grade steel

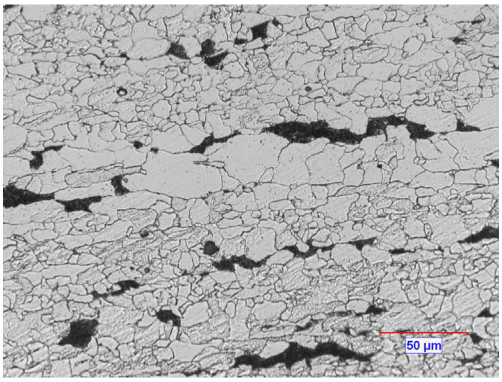


(b) Higher grade steel

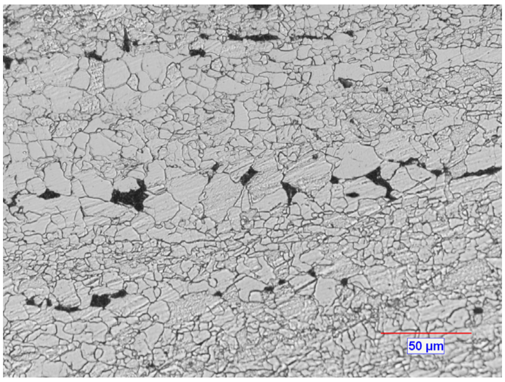
Fig. 9. HIC properties of tested steel

and higher grade steel (No. 2, 4, 6, 8). Lower grade steel is the air-cooled steel, and higher grade steel is the accelerated cooled steel. Fig. 9 shows the HIC resistance of each specimen. The improvement of HIC resistance by addition of Mo is observed clearly. At air cooled steel specimen, the Mo effect is not shown in the low carbon steel (0.03C), but the positive Mo effect is shown in the high carbon steel (0.05C). Though the Mo effect of higher grade steel is smaller than that of lower grade steel, improvement of HIC resistance by addition of Mo is also observed. This improvement of HIC resistance can be explained by the microstructure change.

Hardenability is improved by addition of Mo, thus proeutectoid ferrite and pearlite formation is retarded, and the lower temperature transformation phase such as bainite is promoted.[6] Mo has two different effects on the HIC resistance of carbon steel. One is improvement of the HIC resistance because Mo disperses the banded structure such as pearlite which is weak in sour condition. Another effect should deteriorate the HIC resistance by the formation of a low temperature transformation phase of great hardness.[7]

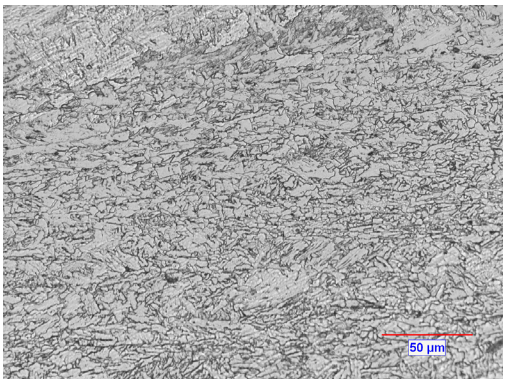


(a)

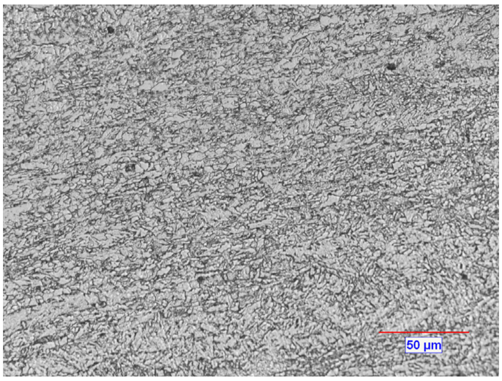


(b)

Fig. 10. Microstructure of (a) 0.05C-0Mo and (b) 0.05C-0.3Mo air cooled plate



(a)



(b)

Fig. 11. Microstructure of (a) 0.05C-0Mo and (b) 0.05C-0.3Mo accelerated cooled plate

The effect of Mo on phase transformation was revealed distinctly in the microstructure observation of air cooled plate as shown in Fig. 10. The fraction of pearlite of Mo added steel is smaller than that of without Mo steel. This suppression of pearlite resulted in the improvement of HIC resistance. In accelerated cooled plate, the microstructure difference between no Mo added steel and 0.3 wt% Mo added steel is not clearly seen as shown in Fig. 11. The acicular ferrite grain size of Mo added steel is smaller than that of no Mo added steel and uniformity of grain of Mo added steel is better than that of no Mo added steel.

4. Summary

Mo is a very attractive element for the linepipe steel for sour service because microstructure of steel is changed extremely by a small amount addition. Especially, in case of cooling capacity after controlled rolling is not enough to control the microstructure, an optimum microstructure for the HIC resistance can be easily obtained by Mo addition. However, the mechanical properties of Mo added steel are sensible to cooling condition. Therefore, at a high Mo added steel, a large deviation of mechanical properties would be a problem for the mass production. The addition of Mo shows a beneficial effect on the HIC resistance because Mo disperses the banded structure which is one of the factors to induce HIC. However, excessive addition of Mo easily generated low temperature transformation phase such as bainite and M/A constituent which is deteriorate the HIC resistance. Therefore, the optimum content of Mo would be determined to satisfy the mechanical and HIC resistance requirements simultaneously. This optimum content of Mo depends on the cooling condition after controlled rolling.

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