The Study on the Susceptibility of Line Pipe Steels to Sulfide Stress Corrosion Cracking

Seong-ung Koh, Kwang Seop Ro*, and Kyoo Young Kim

Pohang Univ. of Science and Technology / Center for Advanced Aerosapce Materials
*Technical Research Center, Pohang Iron & Steel Co., Ltd.

The effect of alloying elements in the line pipe steels on the SSCC susceptibility was studied with respect to hydrogen permeation, crack nucleation, and crack propagation. The micro-alloying elements of Cu-Ni, Mo, and Ti were investigated. SSCC was evaluated using a Constant Elongation Rate Test (CERT) in a NACE TM-01-77 solution. Hydrogen permeation through steel matrix was measured by an electrochemical method. The corrosion current depending on the immersion time in the test solution was determined by linear polarization method as well.

In addition to the basic alloying element, the addition of 0.13wt.% Cu and 0.1wt.% Ni does not show any particular improvement in the electrochemical properties, whereas the addition of Ti reduces the hydrogen permeation by the formation of strong hydrogen trapping sites, Ti-Nb(C,N) precipitates. Addition of 0.13% Mo gives negative effects on two aspects; one is increase in hydrogen flux in steel by inducing pitting in the sulfide film formed on the steel surface and the other is relative easiness in crack propagation due to hard bainitic matrix. As a result, Steel D has the best resistance to SSCC, while Steel B has the highest susceptibility to SSCC.

Keywords : *Alloying element, SSCC, crack nucleation & propagation, corrosion rate, hydrogen permeation.*

1. Introduction

Sulfide Stress Corrosion Cracking (SSCC) is a kind of hydrogen degradation which occurs in the presence of hydrogen sulfide (H_2S) in aqueous solution. Hydrogen sulfide retards the recombination of hydrogen atoms to the molecular hydrogen gas.[1] This poisonous effect accelerates diffusion of atomic hydrogen into the steel leading to catastrophic failure of pipe lines. In SSCC, crack propagation usually occurs perpendicular to the load axis, whereas, in the case of hydrogen induced cracking (HIC), cracking occurs in the form of blisters parallel to the steel surface.[2]

The SSCC process can be divided into three stages; 1) diffusion of atomic hydrogen into the steel, 2) segregation of hydrogen and crack nucleation at steel/defect interfaces under the external load, and finally, 3) crack propagation through the steel matrix.

The diffusion rate of hydrogen in steel matrix is controlled by trapping sites, depending on their size, distribution and binding energy with hydrogen. Titanium is known as one of the most effective alloying elements to decrease the diffusion rate of hydrogen in steel by forming

Ti(C,N) precipitates. The binding energy of Ti(C,N) with hydrogen is 96kJ/mol.[3] Hydrogen diffusion can also be reduced by Cu addition as an alloying element in the steel by forming a protective layer on the steel surface in corrosive media of sour gas environments, so that it decreases the corrosion current at open circuit potential (OCP).[4]

Hydrogen diffusing into steel segregates at defect interfaces in steel, and cracks nucleate at these interfaces, especially at the inclusion/steel interfaces. Elongated MnS inclusion is known to act as the most detrimental defect inducing SSCC and HIC.[5]

Micro-alloying elements such as Cu, Ni, Mo and Ti are often added to HSLA line pipe steels, all of which are added to increase the resistance to SSCC and the mechanical properties. Cu addition over 0.29wt.% can decrease the corrosion rate and the sensitivity to HIC, but addition of 0.3wt.% Ni interrupts such advantages of Cu-bearing steels.[6] The addition of Mo is able to achieve an optimum strength-toughness balance through the formation of fine grained acicular ferrite (low carbon bainite) at relatively low carbon contents, and to reduce the strength loss due to the Baushinger effect by continuous yielding behavior.[7,8] Ti is added to line pipe steels to increase strength

by the formation of precipitates and to retard hydrogen diffusion by trapping.

In this experiment, the effect of alloying elements in the line pipe steels on the SSCC susceptibility was investigated with respect to hydrogen permeation, crack nucleation, and crack propagation. The evaluated microalloying elements include Cu-Ni, Mo, and Ti. The SSCC was evaluated using a Constant Elongation Rate Test (CERT) in NACE TM-01-77 solution. Hydrogen permeation through steel matrix was measured by an electrochemical method, and the corrosion current depending on the immersion time in the test solution was determined by the linear polarization method as well. Test results were analyzed with Optical Microscopy (OM), Scanning Electron Microscopy (SEM), Auger Electron Spectroscopy (AES), image analysis and Vicker's hardness testing.

2. Experimental procedure

2.1 Test steels and specimen preparation

The steels used in the tests are API X60/65 grade steel plates for the line pipe usage. Four kinds of steels with different alloying elements and microstructures were prepared, and their chemical compositions are listed in Table 1.

Steel C contains a basic composition of alloying elements, while the other steels contain additional alloying elements of different kinds. The microstructure of Steel C is mainly composed of ferrite and pearlite. The microstructure of Steel A, which has Cu and Ni as different alloying elements, consists of ferrite and pearlite with a small amount of bainite. Steel D, which contains Ti as an alloying element, has the similar microstructure as Steel A, but its grain size is somewhat smaller than that of Steel A. In contrast, Steel B containing Mo has the microstructure of bainite as a matrix with a small amount of ferrite and pearlite.

Table 1. Chemical compositions of the steels tested

Steel	C	Si	Mn	P	S	Al	N	Ca	Nb	V	Ti	Cu	Ni	Mo
A	0.07	0.21	1.25	0.015	0.001	0.028	0.005	0.0035	0.042	0.019	-	0.13	0.10	-
B	0.062	0.19	1.43	0.01	0.002	0.032	0.0046	0.0031	0.045	0.038	-	-	-	0.13
C	0.045	0.16	0.88	0.007	0.001	0.031	0.005	0.0023	0.039	-	-	-	-	-
D	0.064	0.21	1.38	0.009	0.001	0.024	0.004	0.0012	0.037	0.030	0.013	-	-	-

The steel specimens used for tensile tests are smooth round bars with gage lengths of 25.4mm and diameters of 6.35mm according to the ASTM E 8-93 standard. All specimens were polished up to #1500 SiC paper and

degreased with acetone just before the test.

2.2 Experimental method

2.2.1 Constant elongation rate test (CERT)

The specimen was immersed in a test solution for 96 hours to ensure the HIC in reference to NACE Standard Test Method TM0284-96 and then, pulled in the same solution at a cross-head speed of 0.003mm/min. The test solution used for CERT is NACE TM-01-77 (5% NaCl + 0.5% CH$_3$COOH saturated with H2S) solution. After the test, fracture surface was analyzed with optical microscopy and scanning electron microscopy.

2.2.2 Electrochemical tests

The electrochemical properties of specimens in the test condition were investigated using the potentiodynamic polarization method at a scan rate of 0.166mV/sec. The corrosion current depending on immersion time was determined by the linear polarization method and the surface film formed in the test solution was analyzed with Auger electron spectroscopy after 96 hours of immersion.

2.2.3 Hydrogen permeation test

Hydrogen permeation was measured electrochemically using a Davanathan-Stachurski cell.[9] This cell is divided into two parts, an input part of hydrogen injection and a detection part for measuring the permeation as a hydrogen oxidation current. In the input part, the test solution used was the same as that of CERT, and the potential was not imposed on this part. In contrast, the detection part was filled with a deaerated 0.1N NaOH solution, and 250mV (vs SCE) was imposed to oxidize hydrogen atoms which diffused through the steel specimen from the input part. At the detection part the oxidation current of hydrogen atoms was measured in a potentiostatic condition. The specimen of 1.5 mm thickness was used for this test and groud up to #1500 SiC paper. The specimen was electroplated with palladium to ensure the hydrogen oxidation current just before the setting of the cell circuit. If not, there would be a formation of hydrogen molecules leading to an error of detection current.

3. Results

3.1 Constant elongation rate test (CERT)

To evaluate the susceptibility of steels to SSCC, the resistance of steel to SSCC was determined as the ratio of fracture energy in a test solution to that in ambient air, $E_{f,sol}/E_{f,air}$. Among the four kinds of steels, Steel D showed the highest resistance to SSCC, whereas steel B was the most susceptible to SSCC as shown in Figure 1. By comparing with Steel C which can be regarded as a reference specimen, addition of Cu-Ni (Steel A) and Mo
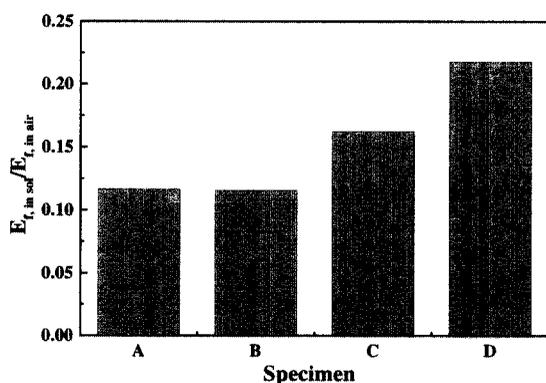
Fig. 1. Susceptibility to SSCC in CERT of tested specimens.

Fig. 3. Polarization curves of the specimens in NACE TM-01-77 solution.

(Steel B) as alloying elements did not increase the resistance to SSCC, but rather decreased the resistance to SSCC. The addition of Ti in steel was helpful to increase the resistance of steel to SSCC

After the test, the fracture surface and crack path were analyzed with scanning electron microscopy and optical microscopy. Two components of cracking, one perpendicular and the other parallel to the direction of the loading axis were observed. The parallel crack along the load axis is a general characteristic of stress oriented HIC (SOHIC) or Type I SSCC.[10] On the other hand, the cracking perpendicular to load axis is called as Type II SSCC which explains the main failure mechanism of steels with a yield strength in excess of 550MPa.[11]

From the fractography, it is shown that cracks typically nucleate at the nonmetallic inclusions and propagate to the steel matrix perpendicular to the load axis in the form of quasi-cleavage fracture as shown in Figure 2. Elongated MnS was not found in the tested samples, but other nonmetallic inclusions acted as the crack nucleation sites.

3.2 Electrochemical tests

The electrochemical properties of the specimens were tested with the potentiodynamic polarization method in the same solution as the one used for CERT. As shown in
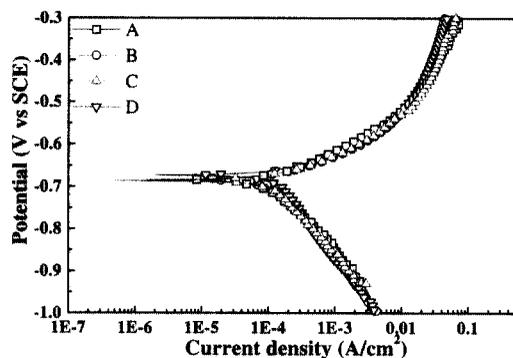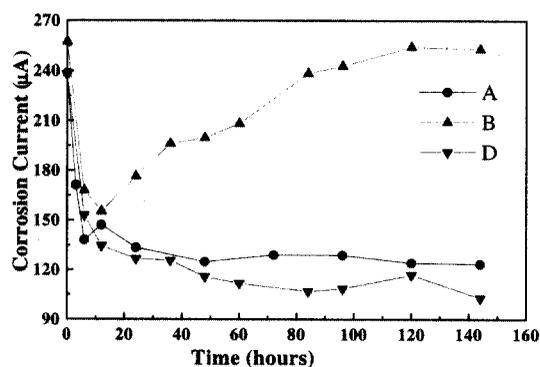

Fig. 4. Variation of corrosion current according to immersion time

Figure 3., all 4 steel specimens showed almost identical electrochemical behavior in the test solution. In the case of steel A containing 0.13wt.% Cu and 0.1wt.% Ni did not decrease the corrosion current to any significant amount. Addition of alloying elements in small amounts seems to have no discernible effect on the dissolution rate of specimens. But after 96 hours of immersion, a thicker surface film was formed on Steel B compared to the others.

The measurement of corrosion current according to immersion time was measured for Steels A, B and D. As

Fig. 2. SEM and OM micrographs showing typical crack nucleation sites and propagation paths.

shown in Figure 4., the corrosion current of steels A and D decreases as the immersion time increases and then remains at a constant value of about 120μA/cm². But in the case of Steel B, the corrosion current decreases until 12 hours of immersion and then increases up to a maximum value of 240μA/cm². This difference is considered to be due to a difference in the surface film characteristics.

3.3 Surface film analysis

Surface film formed in a test solution was analyzed with Auger electron spectroscopy at a sputtering rate of 388 Å /min after the immersion of specimens for 96 hours in a test solution. In the case of Steel A and D, the surface film thickness formed in test solution does not exceed 1μm like Steel C. The surface film is composed mainly of Fe, O, C and S with a little amount of alloying elements. The amount of alloying element in the surface film of Steel A, which contains 5 atomic % of Cu, is significantly larger than Steels C and D, but this amount of Cu in the surface film did not provide any beneficial effect on the corrosion property in the test solution as shown in Figure 3. Figure

5 shows the composition of the surface film of steels formed after 96 hours of immersion in test solution. The surface film of Steel B is about 5(m thick and consists of Fe, O, C, S and 7 atomic % of Mo, which is very large compared to that of base metal. This implies that 0.13wt.% Mo addition decreases the corrosion properties of steel in test solutions as can be expected from Figure. 4 and Figure. 5.

3.4 Hydrogen permeation test

Diffusion of hydrogen, along with the inclusions, is one of the most important parameters to control the SSCC susceptibility, because cracking is accelerated after the ingression of hydrogen at defect sites such as inclusions, grain boundary and voids. Figure. 6 shows the hydrogen permeation current in four kinds of steels according to immersion time until a steady state current is acquired. Steels A and B have the higher permeation current than Steels C and D, which means that the amount of hydrogen diffused into the steel is larger in Steels A and B. In this test, Steel D has the lowest steady state current of 50μ A/cm², which is almost half of that of Steels A and B.
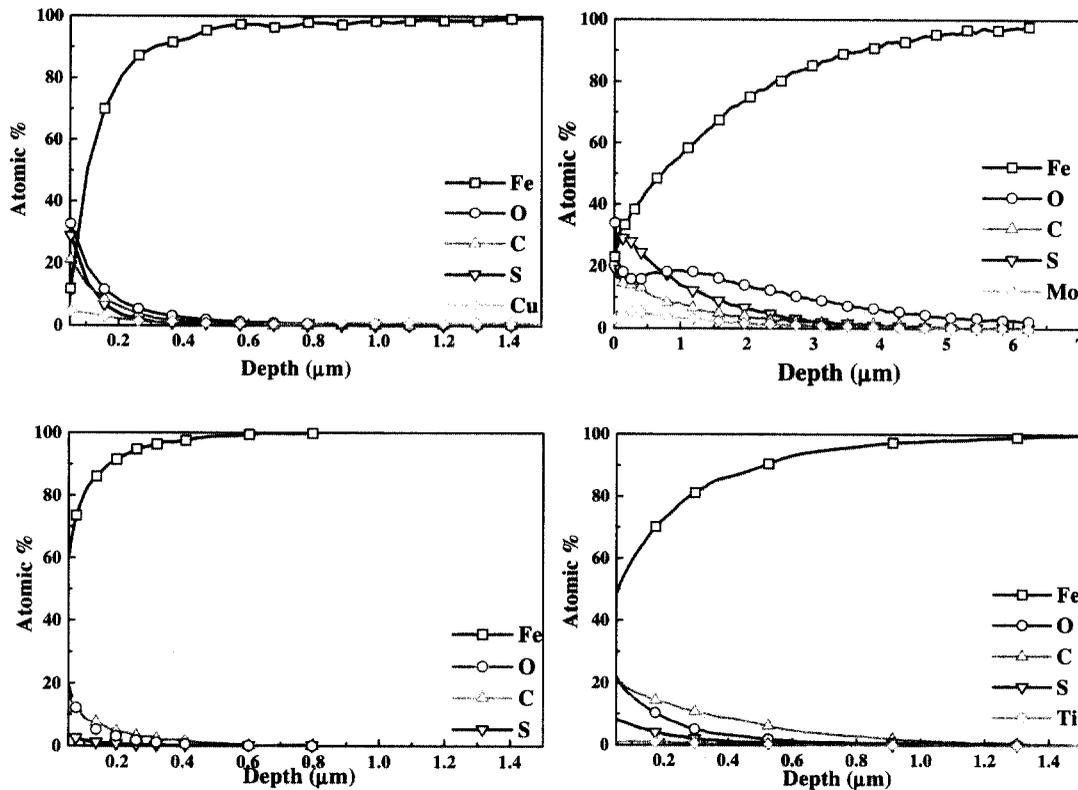

Fig. 5. AES depth profile of surface film formed after 96 hours of immersion.
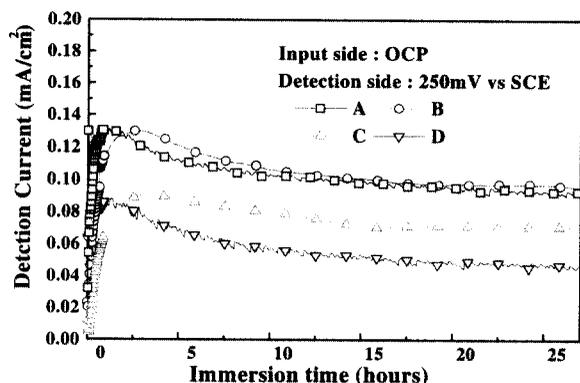
Fig. 6. Hydrogen permeation current at detection side with the input side at OCP in test solution.

4. Discussion

The aim of this study is to evaluate the susceptibility of line pipe steels to SSCC depending on their alloying elements. Factors which affect the SSCC susceptibility of steels can be divided into three kinds according to SSCC mechanisms, which consist of hydrogen diffusion, crack nucleation, and crack propagation. Therefore these 3 factors can be evaluated by examining the hydrogen flux in steel, crack nucleation rate and crack propagation rate. By controlling these factors with optimum level, resistance of steels to SSCC can be obtained.

4.1 hydrogen diffusion in steel

Hydrogen diffusion in steel is influenced by two components. One is the concentration of hydrogen at the steel surface and the other is hydrogen trapping sites in steel, which are closely related to corrosion current at the surface and defects such as solute atoms, vacancies, inclusions, grain boundaries and precipitation in steel, respectively.

In previous studies, it was found that hydrogen permeation is a diffusion-limited process over the specimen thickness of 0.6mm. This means that hydrogen concentration on the surface hardly affects the hydrogen flux in elastic region. But in the real case of SSCC, as the surface hydrogen concentration increases, susceptibility to SSCC increases by the enhanced transport of hydrogen along with moving dislocations in plastic region.[11]

In general, hydrogen embrittlement is enhanced by the nucleation of cracks at defect sites. On the other hand, these defects may also reduce the susceptibility to hydrogen embrittlement by retarding the transport of hydrogen atoms depending on their shape, distribution and binding energy with hydrogen. From the work of Lavi et al.[12], it appears that uniformly distributed precipitations smaller than 10nm in diameter increases the resistance to SSCC

Fig. 7. (a) Current variation of Steel B at 650mV vs SCE, and (b) pitting observed on the surface after test.

of steels.

From Figures 3 and 4, electrochemical properties of the tested samples are not different at the initial stage of immersion in the test solution. But, as the immersion time increases, the variation in corrosion current of Steel B shows the different behavior compared to those of Steels A and D. The corrosion current of Steel B in a steady state was twice as high as that of Steel D, which means that the concentration of surface hydrogen is higher in the case of steel B. An increase in the corrosion current of Steel B may be due to pitting corrosion occurred in the surface as shown in Figure 7. As can be expected, the higher the concentration of hydrogen at the surface, the larger the amount of hydrogen which enters the steel along with dislocations when the specimen is deformed. As shown in Figure 5, a thick surface film formed on Steel B after 96 hours of immersion contains 7 at.% of Mo, The addition of 0.13wt.% Mo seems to decrease the corrosion properties of steel in test solution. If only dissolution rate is taken into consideration, Steel B is considered to be most susceptible to SSCC because its corrosion current is the highest.

The other factor affecting hydrogen diffusion is trap

shape and distribution are assumed to be constant in all specimens, the amount of inclusions in steel is considered to be proportional to the nucleation rate of crack. The amount of inclusions in tested specimens is shown in Table 2.

Table 2. Area fraction of inclusions

	Steel A	Steel B	Steel C	Steel D
Area fraction (R$_i$)	4.0E^{-4}	4.0 E^{-4}	4.6 E^{-4}	2.0 E^{-4}

From this result, the crack nucleation rate of Steel D is considered to be the lowest among four kinds of specimens.

The crack propagation rate is thought to be dependent on the hardness of steel matrix, since most cracks propagate through the steel matrix as shown in Figure 2. It would be expected that the harder the steel matrix, the easier the crack propagation, if other factors are assumed to be fixed. Table 3 lists the hardness values of all 4 steels. Since Steel C shows the lowest hardness value, the resistance of Steel C to brittle crack propagation will be highest, whereas that of Steel B is the lowest since it shows the lowest hardness value.

Table 3. The Vicker's hardness value of the steels tested (300gf)

	Steel A	Steel B	Steel C	Steel D
Hv	204.16	216.5	166.73	187.63

Factors such as hydrogen flux, the amount of inclusions and the hardness of steel matrix, which affect SSCC susceptibility, are plotted in Figure 9. All parameters are normalized by the values of Steel C which contains the common alloying elements of all 4 steels, and then the sum of such values are divided by 3 to get the average value for all parameters. Figure 9(a) shows the average sum of normalized values for diffusion flux (J), area fraction of inclusion (R$_i$) and hardness value (Hv). Figure 9(b) shows the reciprocal values of normalized E$_{f, sol}$/E$_{f, air}$, which indicates the susceptibility of steels to SSCC.

As shown in Figure 9, Steel D has the best resistance to SSCC. This is attributed to decrease in hydrogen flux and crack nucleation rate since the small increase in crack propagation rate is relatively negligible when compared to the effect of decrease in hydrogen flux and crack nucleation rate. The decrease in hydrogen flux is considered to result from Ti-Nb(C,N) precipitates, of which interaction energy with hydrogen is very high (96kJ/mol). The increase in susceptibility to SSCC in Steels A and B comes from the increase in hydrogen flux and crack propagation rate except the decrease in crack nucleation

Fig. 8. Ti rich Ti-Nb carbonitrides formed in Steel D

sites, which retard hydrogen transport in steel. There are two kinds of hydrogen trap sites, one is reversible and the other irreversible.[13] In steel D, Ti-Nb(C,N) precipitates which have a high binding energy with hydrogen seem to reduce the hydrogen flux (J) in steel matrix as shown in Figure 6 and Figure 8, and consequently, they increase resistance to SSCC.

If only hydrogen diffusion is taken into consideration in SSCC, Steel B is considered to be most susceptible and Steel D to be most resistant to SSCC as is shown in Figures 4, 5, and 6. These results are also in good agreement with the CERT result shown in Figure 1.

4.2 Crack nucleation and propagation.

From the work of Takao Aoki et al.[14], SSCC proceeds discontinuously on a microscopic scale. Crack nucleates at the triaxial stress field behind the crack tip because hydrogen concentration is highest in this region. As the defects at which crack can nucleate increase in this region, the probability of crack nucleation will increase. Crack propagation occurs in the direction of the crack tip surface, but if propagation energy is consumed by blunting, propagating cracks will stop before the linkage with other cracks.

As shown in Figure 2, in SSCC, cracks nucleate mainly at nonmetallic inclusions. This means that amount of nonmetallic inclusions can affect the SSCC susceptibility of steels by increasing the crack nucleation rate. If size,

aspects; one is increase in hydrogen flux in steel by inducing pitting in the sulfide film formed on the steel surface and the other is relative easiness in crack propagation due to hard bainitic matrix. Consequently, Steel B has the highest susceptibility to SSCC.

3. In addition to the basic alloying element, addition of 0.13wt.% Cu and 0.1wt.% Ni does not show any particular improvement in the electrochemical properties.

Fig. 9. The parameters which affect the SSCC susceptibility.

rate, which is small compared to the increase of hydrogen flux and crack propagation rate.

5. Conclusions

The effect of alloying elements (Cu-Ni, Mo, and Ti) in the line pipe steels on the SSCC susceptibility was studied with respect to hydrogen permeation, crack nucleation, and crack propagation, and the results are summarized as follows.

1. The addition of Ti reduces the hydrogen permeation by the formation of strong hydrogen trapping sites in the form of Ti-Nb(C,N) precipitates, which explains the best resistance of Steel D to SSCC.

2. Addition of 0.13% Mo gives negative effects on two

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