CORROSION SCIENCE AND TECHNOLOGY, Vol.4, No.2(2005), pp.39~44

Effect Mo Addition on Corrosion Property and Sulfide Stress Cracking Susceptibility of High Strength Low Alloy Steels

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The purpose of this work is to understand the effect of Mo addition on SSC susceptibility of high strength low alloy steels in terms of microstructure and corrosion property. Materials used in this study are high strength low alloy (HSLA) steels with carbon content of 0.04wt% and Mo content varying from 0.1 to 0.3wt%. The corrosion property of steels was evaluated by immersion test in NACE-TM01-77 solution A and by analyzing the growth behavior of surface corrosion products. SSC resistance of steels was evaluated using constant load test. Electrochemical test was performed to investigate initial corrosion rate.
Addition of Mo increased corrosion rate of steels by enhancing the porosity of surface corrosion products. However, corrosion rate was not directly related to SSC susceptibility of steels.

Keywords *: HSLA steel, Mo, corrosion property, corrosion product, SSC susceptibility*

1. Introduction

Requirement for the performance of linepipes to transport prime energy sources has become diversified and stringent as the exploration of oil and gas fields is expanding toward severe environments such as the deep sea and Alaska. During transportation of oil and natural gas through API grade steel pipe, hydrogen sulfide (H_2S) environment in petroleum and natural gas generates various engineering problems such as brittle cracking of steels, which is related to hydrogen atoms.[1)] Hydrogen related cracking can be classified into two categories; hydrogen induced cracking (HIC) and sulfide stress cracking (SSC). Even without applied stress, HIC or blistering occurs at hard phase constituents and non-metallic inclusions by diffused hydrogen. And this cracking develops mainly parallel to the steel surface and sometimes in a stepwise pattern. In the presence of applied stress and residual stress, SSC occurs at the place subjected to stress and develops almost perpendicularly to the stressed direction.[1)-5)]

Because of increasing demand for oil/gas transportation efficiency, linepipe steels are required to have high strength and low-temperature toughness as well as corrosion resistance against sour gas environments.[6)] In general, to increase the strength and toughness of steels, the addition of alloying elements such as Cr and Mo is used. These elements can increase the A_3 temperature, decrease the B_s and M_s temperatures and delay the transformation of ferrite and pearlite. Thus, addition of Cr and Mo was characterized to increase hardenability and formation of the low-temperature transformation structure such as martensite/austenite (M/A) constituents.[3)] The addition of these elements results in the reduction of the brittle cracking resistance. Mo addition is more detrimental to brittle cracking than Cr addition due to its higher capacity to form low temperature transformation structure.[6)-8)] However, in some HSLA steels containing 0.3% Mo, fine dispersed precipitate configuration has been created, hence improves SSC resistance of steels.[7),9)-10)] Especially, Mo in low carbon steel is one of the most effective alloying elements to achieve the optimum strength-toughness balance by forming fine grained acicular ferrite microstructure. Another merit of Mo-bearing steel is its continuous yielding behavior, which can alleviate strength loss due to the Bausinger effect during pipe forming.[11)-12)]

Acicular ferrite matrix with a small amount of polygonal ferrite is one of the most attractive candidate microstructures for pipeline steels because of its optimal com-

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bination of high strength and good toughness. This microstructure contains high density dislocations and is inherently fine grained due to its relatively low transformation temperature,[13)-15)] accordingly, it can offer the potential for improving the strength and toughness.

The purpose of this work is to understand the effect of Mo addition on SSC susceptibility of high strength low alloy steels in wet H_2S environment in terms of microstructure and corrosion behavior.

2. Experimental procedure

2.1 Material

The materials used in the tests were HSLA steels with carbon content of 0.04wt%. Detailed chemical composition is listed in Table 1.

Table 1. Composition of test steels (wt%)

No.	C	Si	Mn	Others	Mo
A1	0.04	0.2	1.3	Nb, V, Ti, Ca	-
A2					0.1
A3					0.2
A4					0.3

Mo content varies in range from 0 to 0.3 wt% and all the other alloying elements are identical. The thermo-mechanically controlled rolling process (TMCP) conditions are also identical for all steels.

2.2 Corrosion properties

To evaluate the corrosion behavior of test materials in sour environment, both linear polarization and immersion test were carried out in H_2S saturated NACE-TM01-77 solution A. Dimension of all specimens was 25 ± 0.05 mm x 25 ± 0.05 mm x 6.0 ± 0.05 mm. They were ground up to #1500 SiC paper and weighted. Ground specimens were degreased with acetone before immersion in H_2S saturated NACE-TM01-77 solution A (water 1890g + Acetic acid 9.95ml + 100g NaCl). The specimens were taken out of the test solution after immersion periods of 10, 20, 45, 95 and 165 hrs respectively, and weight loss was measured after removal of corrosion product. To analyze corrosion product, optical microscopy (OM), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) were used. XPS analysis was performed using an EscaLab 220-IXL. All samples were analyzed for the same position corresponding to angles 30° and 90° between the surface normal and the cylindrical mirror analyzer axis. For the curve fitting process, Gaussian-Lorentzan formula and background elimination of Shirly were used. The

Table 2. The binding energy of the chemical species

Chemical Species		Binding Energy (eV)
S_{2p}	S	164
	FeS	161.6
	FeS_2	162.9
	MoS_2	162.5
Mo_{3d}	Mo	228
	Mo^{4+}	229
	Mo^{6+}	232.6
$*S_{2s}$	MoS_2	227.31

various binding energies for S_{2p} and Mo_{3d} levels are summarized in Table 2.

To investigate the growth behavior of corrosion product, open circuit potential (OCP) and roughness measurements were performed.

2.3 Microstructual characterization and mechanical properties

Microstructure was examined primarily by using OM and SEM. Second phases were observed using SEM and energy disperse spectroscopy (EDS). The specimens were ground up to #2000 SiC paper and then polished with 1 μm diamond suspension. Specimens were degreased with acetone and etched with a natal solution (5% HNO_3 + CH_3OH).

Mechanical properties were examined by constant elongation rate test (CERT). CERT method was used to determine yield strength. Specimens were pulled at a crosshead speed of 5mm/min.

2.4 Constant load test (CLT)

To evaluate SSC resistance, the CLT was performed in reference to NACE standard test method TM-01-77-96 A. Round bar tensile specimens were ground up to #2000 SiC paper and then micro-polished with 0.25μm diamond suspension.

3. Result and discussion

3.1 Microstructual characterization and mechanical properties

Fig. 1 shows the typical microstructure of test materials. All steels consisted of quasi-polygonal ferrite (QPF), fine grained acicular ferrite (AF) and small amount of secondary phases such as M/A constituent and pearlite. As Mo content increases, area fraction of QPF decreases and that of AF increases.

Effect of Mo on mechanical property of steels is

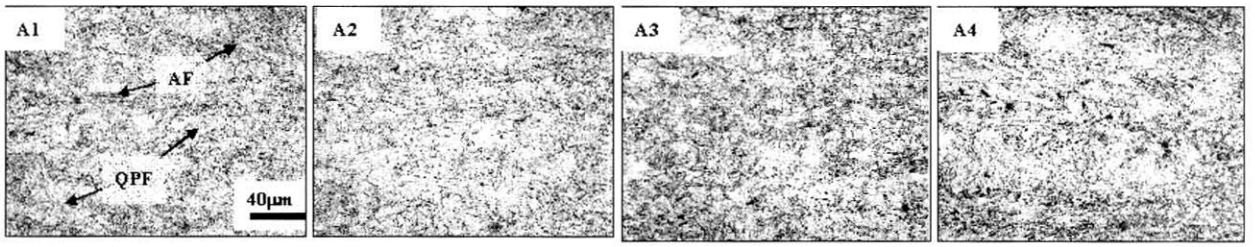


Fig. 1. Microstructure of tested steels

demonstrated in Table 3. Table 3 shows that addition of Mo increases yield strength (YS) and ultimate tensile strength (UTS) of tested steels. From behavior of stress-strain curves and characterization of microstructure, it can be concluded that addition of Mo delays transformation of ferrite and encourages the formation of low temperature transformation structure such as AF and M/A constituent. This is consistent with results reported by other investigators.[6)-8)]

Table 3. Mechanical properties of tested steels

	Yield strength (kg/mm^2)	Ultimate tensile strength (kg/mm^2)
A1	55	63
A2	54.5	63.5
A3	57.5	67
A4	58.5	68

3.2 Corrosion behavior of test materials in sour environment

As for the initial corrosion property, increase in corrosion rate is significant for Mo-added steels as shown in Fig. 2(a). This result means that addition of Mo increases dissolution rate of steel at the early stage and is consistent with the result made by weight loss measurement as shown in Fig. 2(b).

Fig. 3 (a) shows cross-sectional SEM image after 720hrs of immersion in sour environment. It reveals that the corrosion product on 0.3wt% Mo added steel (A4) is thicker than that on Mo free steel (A1). SEM photos shown in Fig. 3(a) reveal crack along the interface between corrosion product and substrate. The crack may develop due to the loss in coherence at the interface. Fig. 3(b) is EDS line profile for the cross-section of A4 after 720 hours immersion. The corrosion product is composed mainly of FeS_2, but it seems that Mo was not detected due to its small content.

In general, corrosion products are formed by following reactions;

Anodic $\quad Fe \rightarrow Fe^{2+} + 2e^-$

Cathodic $\quad H_2S + e^- \rightarrow H + HS^-$

$\quad H_2S + H + e^- \rightarrow H_2 + HS^-$

$\quad H^+ + e^- \rightarrow H$

Film formation $\quad Fe^{2+} + 2HS^- \rightarrow FeS_2 + H^2$

From XPS analysis on the rust layer of Steel A4 formed

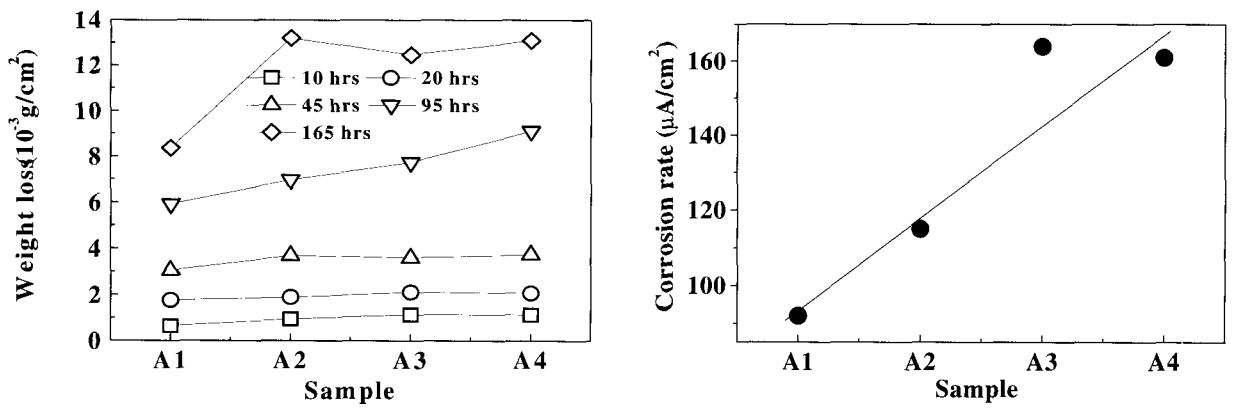
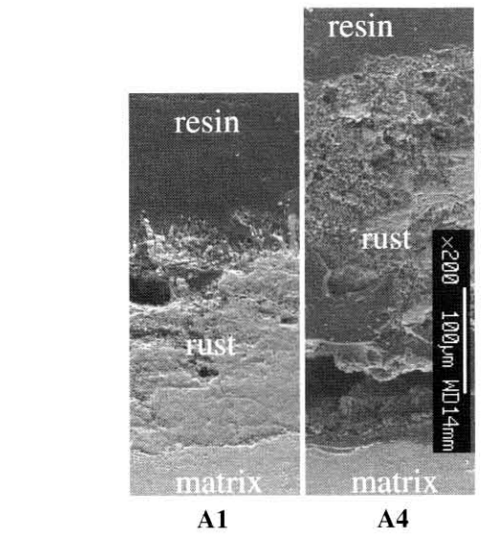
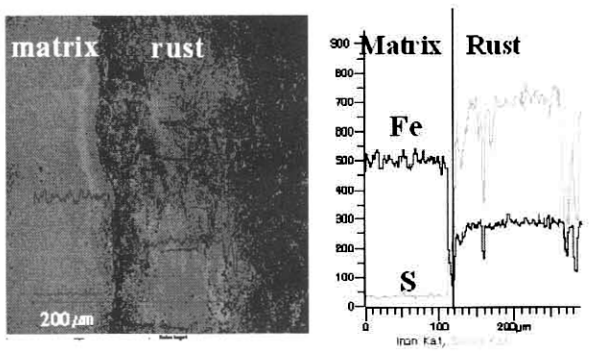


Fig. 2. Corrosion rate; (a) current density determined by linear polarization, (b) weight loss change by immersion time



(a)



(b)

Fig. 3. (a) cross-sectional view of corrosion products for Steels A1 and A4 and (b) EDS line profile for rusted Steel A4

after 3 hrs' immersion, formation of MoS_2 was confirmed in outermost part of rust layer from Mo_{3d} spectra as shown in Fig. 4.

Because of difference in atomic radius between Fe (= 0.124 nm) and Mo (= 0.136 nm), MoS_2 in iron sulfide film can decrease the stability of iron sulfide on steel surface. Then, the corrosion rate of Mo added steels becomes higher than that of Mo free steel.

3.3 Sulfide stress cracking in sour environment

Fig. 5 shows time to failure of tested steels at a sustained load equivalent to percentage of actual YS. SCC threshold stress is over 90% of actual YS for Steel A4 and 80% for the others. From this result, SSC resistance seems not to be directly related with Mo content in steels and corrosion rate as can be seen from Fig. 6.

Fig. 7 shows fractography of failed specimens after SSC testing. Cracks nucleate at M/A constituent and non-

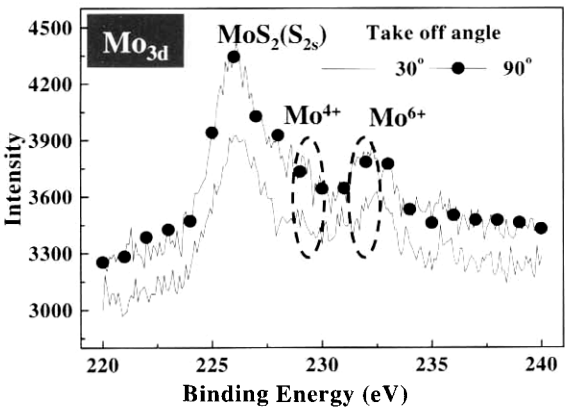


Fig. 4. Mo_{3d} XPS spectra on the rust layer of Steel A4 formed after 3 hrs immersion

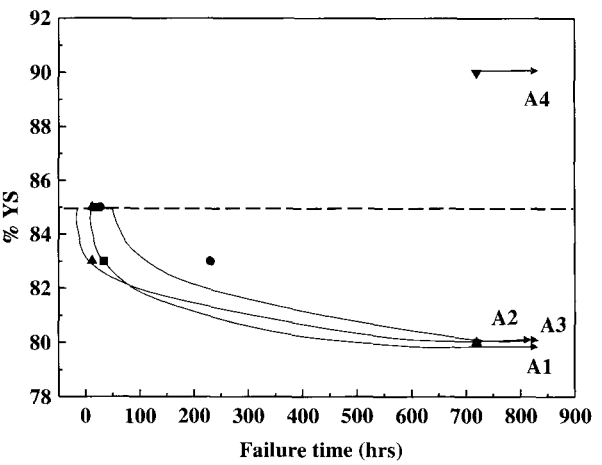


Fig. 5. SSC threshold stress of tested steels

metallic inclusion in a quasi-cleavage manner.

Also, cracks nucleate perpendicular to applied stress and propagate along the plane of maximum shear stress. Fig. 8 shows the area fraction of inclusions for all tested steels.

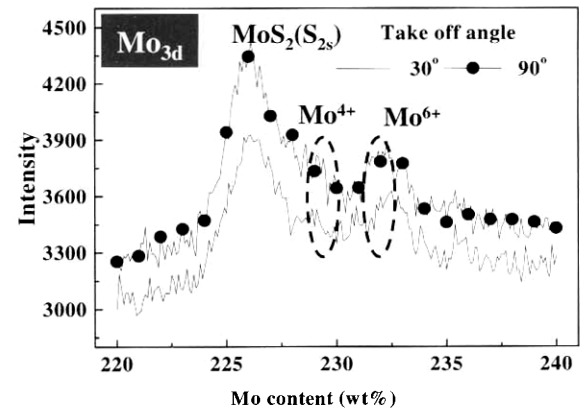
For the most part of inclusion, they are smaller than 5 μm in diameter. Although SSC nucleated at non-metallic inclusions, area fraction of inclusion is not a key parameter for SSC because inclusion size is pretty small (<5 μm)

4. Conclusions

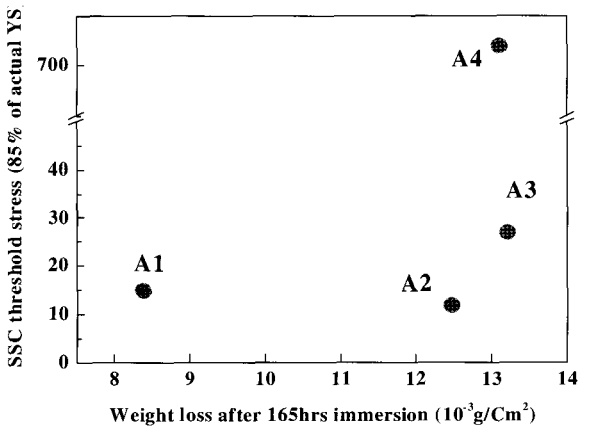
SSC susceptibility of linepipe steels were evaluated in terms of microstructure and corrosion behavior, and the results are summarized as follows:

1. Addition of Mo enhances formation of low temperature transformation structures such as acicular ferrite and M/A constituents therefore improves strength of the steel.

2. Mo addition decreases the stability of sulfide film,

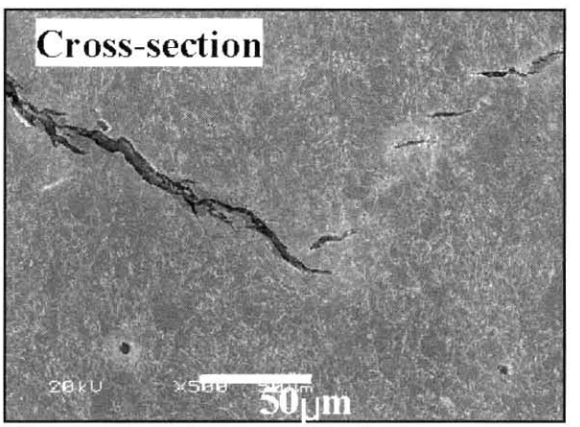


(a)

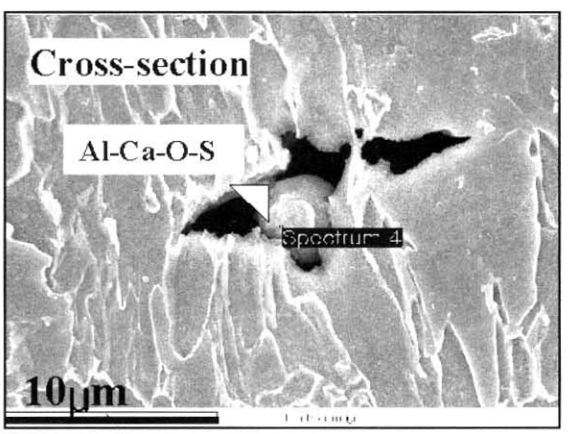


(b)

Fig. 6. Correlation between SCC threshold stress and; (a) Mo content in steels and (b) corrosion rate



(a)



(b)

Fig. 7. Fracture morphology; (a) Cracks nucleated perpendicular to applied stress and propagate along the plane of maximum shear stress, and (b) Cracks nucleated at a non-metallic inclusion

and increases the dissolution rate of corrosion products.

3. Steel A4 containing 0.3 wt% Mo is the most resistant to SSC among all tested steels.

4. Corrosion is significant in Mo-added steels compared with Mo free steel and increase in corrosion rate of Mo-added steel is proportional to Mo content. But, corrosion rate is not directly related with SSC susceptibility of steel.

5. Inclusions smaller than 5 μm in diameter do not seem to affect SSC of tested steels.

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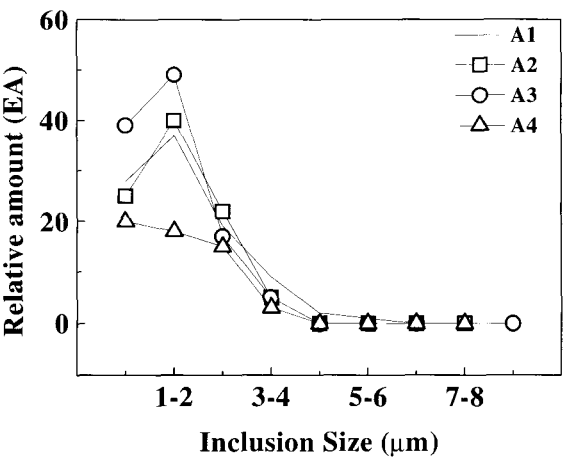

Fig. 8. Distribution of inclusion in test materials

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