JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 15, Preprint 40 submitted 9 October 2012

Hydrogen Sulphide Resistance of high strength line pipe steels in hydrogenated and sour gas media

P. Saravanan[1], Sweta Mishra[2], S. Srikanth[1] and K. Ravi[1]

[1]*Chemical Analysis and Corrosion Engineering Group, R&D Centre for Iron and Steel, SAIL, Doronda, Ranchi, INDIA*

[2]*National Institute of Foundry and Forge Technology, Hatia, Ranchi,INDIA*

sarvan@sail-rdcis.com

Abstract

The API line pipe steels find wide application in offshore oil drilling structures / platforms as well as in cross-country oil and gas line pipes. There is a progressive trend towards development of higher strength line pipe steels in the industry to enable handling and transportation of greater volumes crude oil at higher operating pressures. Higher the strength of the material, higher the susceptibility to hydrogen induced cracking (HIC) & sulphide stress corrosion cracking (SSC). Newly developed API-X65 and API-X70 line pipe steels were characterized with respect to hydrogen induced cracking (HIC) and sulphide stress corrosion cracking (SSC) performance in sour gas media. API-X65 and API-X70 were microstructurally characterized. Electrochemical studies (both polarization and electrochemical impedance spectroscopy) were carried out in sour gas media to understand the corrosion mechanism. The CSR, CLR and CTR were evaluated as per NACE TM-0284 and found that both the steels are susceptible to HIC failure. SSC studies were carried out as per NACE TM-0177 Method A, to evaluate the threshold stresses (σth) of the steels.

Keywords: Hydrogen induced cracking (HIC), Sulphide stress corrosion cracking (SSC), corrosion, Tafel Extrapolation, and Electrochemical impedance spectroscopy (EIS).

Introduction

API line pipe steels are extensively used in oil and gas transportation pipelines. Line pipe steels have a low price-to-yield strength ratio; with minimum yield strength (σy) of 290MPa are readily available in the oil and gas industry. In addition to material strength, these steels provide good weldability because of their low carbon contents. The approach to generate API steels involves a combination of lower carbon content and fine grain size by microalloying along with thermomechanical rolling or accelerated cooling [1]. API grade steels are designated by their minimum yield strength value. The latter process enabled

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 15, Preprint 40 submitted 9 October 2012

materials up to X70 (σy = 482MPa) to be produced from steels that are microalloyed with niobium and vanadium and have a reduced carbon content. An improved processing method, consisting of thermomechanical rolling plus subsequent accelerated cooling, emerged in the eighties. By this method, it has become possible to produce higher strength materials like X80 (σy = 551Mpa). The X80 has further reduced carbon content and thereby excellent field weldability. Additions of Mo, Cu and Ni enable the strength to be raised to that of grade X100 (σy = 689MPa), when the steel is processed to plate by thermomechanical rolling plus modified accelerated cooling [2].

There is a progressive trend towards development of higher strength line pipe steels in the industry to enable handling and transportation of greater volumes crude oil at higher operating pressures. The higher strength line pipe steels are more susceptible to catastrophic hydrogen-induced failures and extensive sulphide stress corrosion (SSC) cracking in sour gas environments of cross-country pipelines, handling and transporting crude petroleum. There is thus an impending need to evaluate and characterize the hydrogen-induced cracking (HIC) and sulphide stress corrosion (SSC) susceptibilities of the newer high strength grades of line pipe steels in hydrogenated and sour gas media to assess their performance.

Recently, RDCIS had also embarked on the development of API-X65 and API-X70 line pipe steels. Trial productions of API-X65, API-X70 steels have been undertaken at integrated steel plant and the requisite mechanical properties have been successfully met in industrial heats. One of the important aspects to assure good performance of pipeline steels is to minimize cracking susceptibility when exposed to sour environments. Hence, the present work focuses on characterization of newly developed API X65 and 70 line pipe steels on terms of HIC and SSC phenomenon in sour gas media.

EXPERIMENTAL

Materials

Two grades of micro alloyed hot rolled coils of API-X65 and X70 steels were collected for studies. Their chemical compositions were analyzed by optical emission spectrometer (OES) Model-THERMO, ARL 3460 and represented in the Table-1.

Microstructure Characterization

For micro structural characterization, the collected steels were cut into small samples around 10mm X 10mm dimension. The samples were hot mounted using conducting

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 15, Preprint 40 submitted 9 October 2012

resin and metallographically polished using SiC paper of different grade and finally with 1μm alumina powder. To reveal the microstructure, the specimens were then etched with 2% nital and observed in optical microscope Model-REICHERT MeF2.

Table-1. Material Composition in wt%

Steels	C	Mn	S	P	Si	V	Nb	Ti
API-X65	0.08	1.29	0.008	0.024	0.31	0.05	0.038	---
API-X70	0.09	1.41	0.009	0.013	0.38	0.0477	0.047	0.022

The mechanical properties of the steels were evaluated using Instron machine Model-1195 at a constant ramp speed of 2 mm/min. Flat tensile specimen of 50 mm gauge length was used for the test.

Electro Chemical Corrosion Studies

Tafel Extrapolation Test

For investigating the corrosion performance of collected line pipe steels Tafel Extrapolation experiments were performed in 7N H_2SO_4 + 1 g 1/l thiocarbamide solution using a computer controlled Versa STAT MC multichannel potentiostat. The above solution (7N H_2SO_4 + 1 g 1/l thiocarbamide solution) is equal to the NACE (National association for corrosion engineers) solution (5% NaCl and 0.5% CH3COOH) [3]. A standard PAR model K0235 flat electrochemical corrosion testing cell with a platinum (Pt) wire mesh counter electrode and a silver-silver chloride [Ag, AgCl/ KCl (saturated); Eo = +0.197 V versus SHE] reference electrode were conjunctively employed for the experiments. Prior to testing, the steels were metallographically polished to 0.5 μm using alumina suspension. The experiment was conducted at the potential scan rate of 0.5mV/s using Versa Studio Research Electrochemistry Version 1.42.

Electrochemical impedance spectroscopy

The collected line pipe steels were metallographically polished as described earlier, and subjected to electrochemical impedance spectroscopy (EIS) in 7N H_2SO_4 + 1 g 1/l thiocarbamide solution [3] in order to characterize the impedances of the films formed on steels. For the EIS experiments, the same standard flat electrochemical corrosion testing cell with a Pt wire mesh counter electrode and a silver-silver chloride reference electrode was used. The three-electrode corrosion cell was electrically connected to Versa STAT MC multichannel potentiostat, with EIS. The impedance spectra generated in the form of complex plane Nyquist impedance plots were regressed and modeled with their equivalent electrical circuit, R(QR) using ZSimpwin® software, developed by PAR Version 3.21, to compute the charge transfer resistances (in Ω.cm2) and capacitances (in F/cm2) of the films.

Hydrogen Induced Cracking (HIC) Studies

HIC test was done as per the NACE TM-0284 [4] standard procedure in the NACE solution A. The sample were immersed in a solution of 5% NaCl and 0.5% CH3COOH saturated with hydrogen sulphide gas for a period of 96h. The HIC test samples were prepared according to the standard NACE TM-0284. After immersing the test sample and sealing the test vessel, the vessel was purged by nitrogen for at least 1 hour at a rate of 100cc/min to eliminate oxygen. The test gas (H_2S gas) was bubbled through test solution at a rate of 200cc/min for the first 60 min, thereafter a +ve pressure of H_2S gas was maintained. Initially the pH of the solution was maintained in the range of 2.7 ± 0.1. After the test, final pH was measured (final pH should be within 4) and samples were rinsed with water, followed by wire brushing to remove all loose scale and corrosion products. The samples were then sectioned at 25mm interval and metallographically polished and viewed for cracks under 100X magnification using optical microscope. If the cracks were not visible then the samples were etched slightly with 2% Nital solution. The Crack sensitivity ratio (CSR) and Crack length ration (CLR) and Crack thickness ratio (CTR) were determined as per NACE TM-0284.

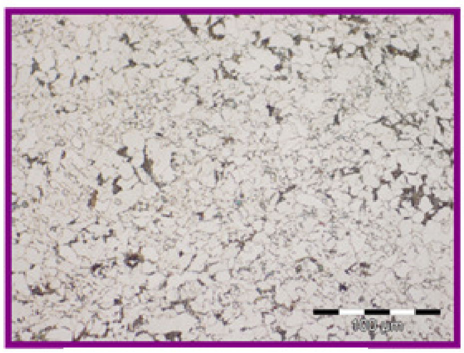
Sulphide Stress Corrosion (SSC) Studies

SSC experiment was performed as per NACE Standard TM-0177 [5], tensile samples were subject to constant load (Proof Ring) and immersed in a solution of 5% NaCl and 0.5% CH3COOH saturated with hydrogen sulphide and the delayed failure characteristics are determined. The test specimens were loaded under uniaxial tension by compressing the proof ring. Amount of deflection needed to apply the desired load with the proof ring was determined by using the calibration curves of each proof ring. Load for stressing the specimens were determined by $P = S \times A$, where P = Load, S = applied stress and A = actual cross section area of the gauge section. The specimens were loaded at stress values equivalent to different percentages of the material's yield strength values. The corresponding time to failure (TTF) was recorded by an automatic timer attached to the test specimens. The time to failure is determined for a maximum test period of 720h (30 days). The cracking susceptibility was expressed in terms of a threshold stress (σth) for SCC below which cracking did not occur during the maximum test duration. Initially the pH of the solution was maintained in the range of 2.6 to 2.7 and test was discarded if exceeds 4 after the test.

RESULTS AND DISCUSSION

Microstructure Characterization

Microstructure of the API-X65 and X70 steels shown Figure 1, have ferrite-pearlite microstructure of different grain size. The API-X70 steel showed fine grain microstructure with average grain size of about 4 to 6µm, where as API-X65 showed the average size of about 15 to 20 µm. As seen from the Table 1. There is not much difference in the chemical composition between two alloys; the controlled rolling might have caused difference in the grain size.



API X65

API X70

Figure 1 Microstructure of API-X65 and API-X70 Line pipe steels

The mechanical properties of the API-X65 and X70 steels were given in the Table 2. As expected yield strength and ultimate tensile strength are higher for fine grained steels (API-X70) than that of the (API-X65) steels. Due to increase in the strength, elongation decreases from 27 (API-X65) to 23 for (API-X70).

Table-2. Strength of API grade steels

Steels	Yield Strength		Ultimate Tensile Strength		% Elongation
	Mpa	Psi	Mpa	Psi	
API-X65	513.87	74,531	610.28	88,514	27.89
API-X70	572.96	83,101	650.30	94,275	2460

ISSN 1466-8858 Volume 15, Preprint 40 submitted 9 October 2012

Electrochemical Corrosion Studies

Tafel Extrapolation Test:

Table 3, shows the results of Tafel polarization of experiments of (Figure 2) API-X65 and X70 steels in 7N H_2SO_4 + 1 g 1/l thiocarbamide. It is clear from the plot that there is not much difference in corrosion behavior of the two alloys. The API-X70 steel showed lower corrosion rate (93mpy) compared to that of API-X65 steel (128mpy). It is interesting to note from the polarization plot that anodic and cathodic Tafel's slope is more or less equal. This behavior might be due to absorption phenomenon of hydrogen species to the surface of the metals, which will be studied later [6].

Table-3. Electrochemical polarization parameter of API-X65 and API-X70 Line pipe steels in Sour gas environment

Steels	**Corrosion potential Vs AgCl (mV)**	**Anodic Tafel Slope (βa) (mV per decade of A/cm^2)**	**Cathodic Tafel Slope (βc) (mV per decade of A/cm^2)**	**Corrosion Rate (mpy)**
API-X65	-485	91.6	136.6	128
API-X70	-475	84.8	142.9	93

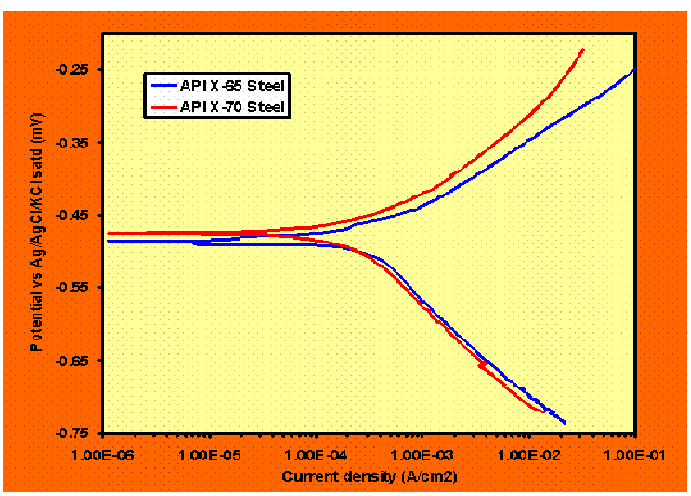


Figure 2 Electro chemical Polarization Plots of API-X65 and API-X70 Line pipe steels in Sour gas environment

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 15, Preprint 40 submitted 9 October 2012

Electrochemical impedance spectroscopy

To know the physical features of the corrosion mechanism, Electrochemical Impedance spectroscopy studies were carried out for both the steels (API-X65 and API-X70) in 7N H_2SO_4 + 1 g 1/l thiocarbamide. Figure 3 shows the EIS plots (Nyquits and Bode Plot) of API-X65 and X70 steels in 7N H_2SO_4 + 1 g 1/l thiocarbamide solution. Film capacitance and charge transfer resistance for the above EIS plot were obtained by fitting the EIS plot with the equivalent circuit using ZSimpwin® software (Figure 3c) and the impedance parameters are tabulated in the Table 4. From the table is clear that API-X70 showed a higher polarization resistance than that of API-X65 as seen in Tafel polarization experiment. From the Nyquist plot it is clear that both the steels showed a negative loop at lower frequency, which corresponds to inductance behavior. Inductive behavior which appears in the high frequency range is fairly easily explained by instrumental artifacts, or by the inductance of the electrode, or the inductance of the connecting wires. Inductive behavior at low frequencies, however, still mystifies many. The most quoted explanation for this low frequency inductive behavior is an adsorption process at the electrode surface. Recently few papers [7 and 8] which deals with inductance, including one which details an instrumental artifact that can yield low frequency inductive behavior. The effect of H2S on the anodic reaction was likely caused by H2S chemisorptions on the metal surface. This catalyzes the anodic discharge reaction as seen in reaction (1, 2 and 3) and generates more anodic current densities for the same potential by reducing the activation energy required for the anodic reaction [9].

$$Fe + H_2S \rightarrow FeHS^-_{ads} + H^+ \qquad (1)$$
$$FeHS^-_{ads} \rightarrow FeHS^+_{ads} + 2e \qquad (2)$$
$$FeHS^+_{ads} + H^+ \rightarrow Fe_2+ + H_2S \qquad (3)$$

Table-4. Electrochemical impedance Spectroscopy parameter of API-X65 and API-X70 Line pipe steels in Sour gas environment

Steels	**Film capacitance $F/cm^2 \times 10^{-5}$**	**Charge transfer resistance $\Omega.cm^2 \times 10^{-5}$**
API-X65	3.078	3.078
API-X70	4.942	4.942

ISSN 1466-8858 Volume 15, Preprint 40 submitted 9 October 2012

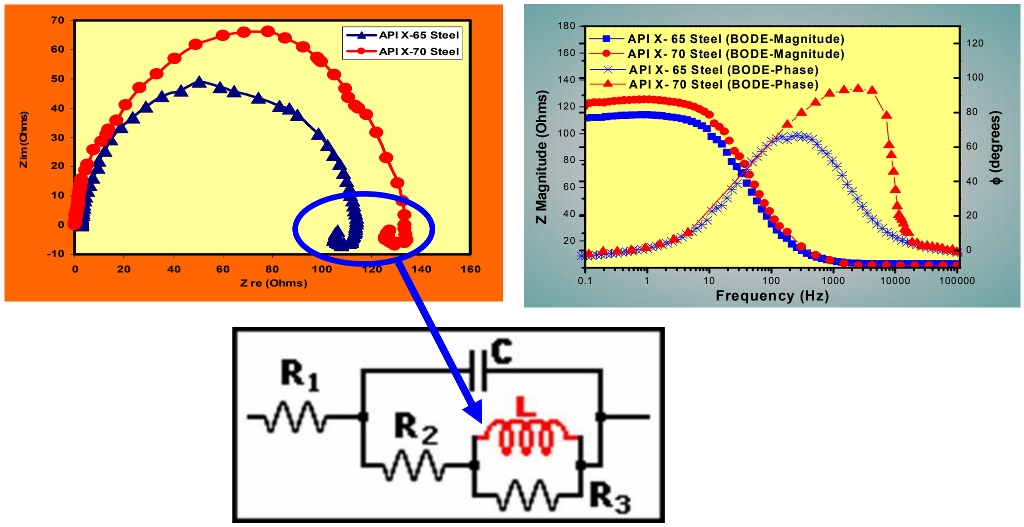


Figure 3 Electro chemical Impedance Spectroscopy studies (a) Nyquist Plots and (b) Bode plots (c) Equivalent circuit for the EIS plot. of API-X65 and API-X70 Line pipe steels in Sour gas environment

Hydrogen Induced Cracking Studies

Figure 4 shows the optical micrograph of the HIC tested samples, from which crack length ratio (CLR), crack sensitivity ratio (CSR) and crack thickness ratio (CTR) were determined and tabulated in Table 5. API-X70 steel showed higher susceptibility to HIC as CSR, CLR and CTR values were larger than that of API-X65 steel. API-X65 showed few cracks, where as API-X70 showed many deep pits, crack propagates along these deep pits. From these studies the CLR and CTR of both the material were found to significantly higher than that of the level specified for sour gas application [Type III class material should have CSR ≤ 2%, CLR ≤ 15% and CTR ≤ 5%]. However, CSR for both the steels was within applicable limit under Type III class for sour gas application. Hence, both the material does not have HIC resistance in sour gas media.

Table 5. Hydrogen induced cracking parameter of API Steel as per NACE TM 0284

	API-X65 Steel (in %)	API-X70 steel (in %)	Acceptable limit for sour gas application (Type III class) (in %)
CSR	0.77	1.4	≤ 2
CTR	6.7	18.9	≤ 5
CLR	57.7	58	≤ 15

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 15, Preprint 40 submitted 9 October 2012

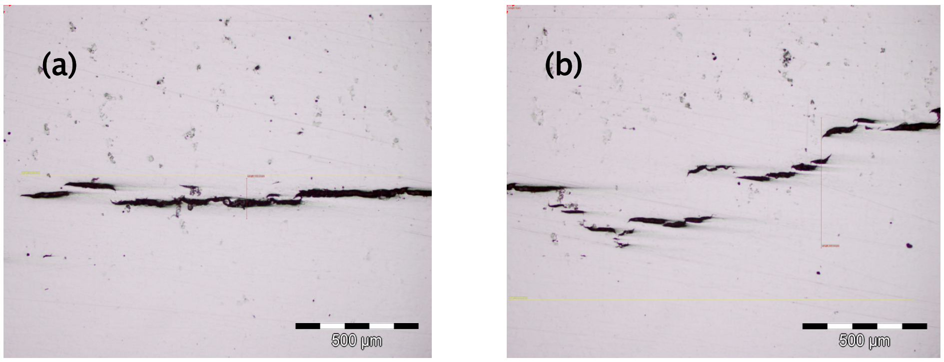


Figure 4 Micro Structure of cracks after HIC studies of (a) API-X65 steel and (b) API-X70 steel as per NACE TM 0284

Sulphide Stress Corrosion Studies

The Sulphide stress corrosion experiments were carried out on API-X65 and API-X70 steels for various percentages of yield strength as per NACE TM 0177 method A. The corresponding time to failure was recorded (Table 6). The SSC test was carried out for maximum period of 720 h. The results from the Table 6 are plotted in Figure 5 for various stress levels. It can be seen that the time to failure increased with decrease in the applied load. In addition, the change of time to failure values between two consecutive applied stresses seemed to widen as the threshold stress value was approached. From the figure it is clear that both the material behave in similar manner, there is not much difference in the behavior of SSC pattern. The threshold stress of API-X65 was found to be 51% approximately of yield strength and API-X70 was about 48% of yield strength. This difference in the threshold stress might have occurred because of difference in the grain size or difference in the strength.

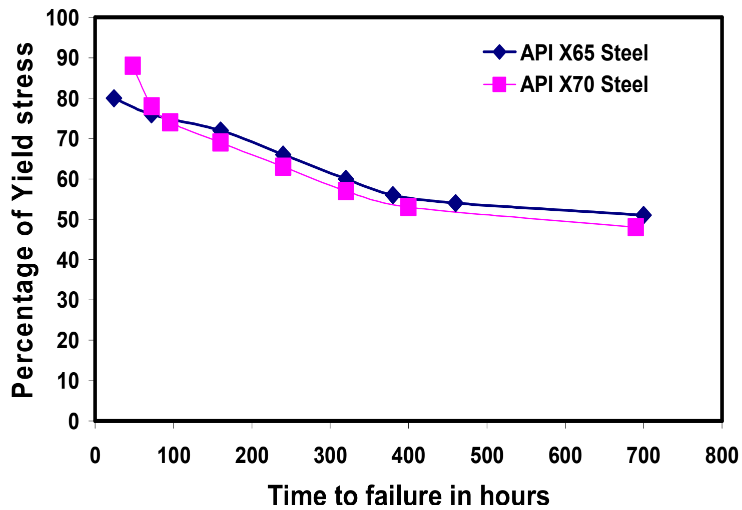


Figure 5 Sulphide stress corrosion cracking (SSC) studies

CONCLUSION

API X65 and X70 steels showed a typical ferrite-pearlite microstructure of different grain size. Electrochemical corrosion studies revealed that in both the steels, the effect of H2S on the anodic reaction was caused by H2S chemisorption on the metal surface. CLR, CSR and CTR were evaluated from HIC studies and found to be significantly higher than the level specified for sour gas application. In SSC test, the threshold stresses were evaluated to be 51% and 48% of the yield stress for API X65 and API X70 steel respectively.

REFERENCES

1 ASM Metals Handbook, Properties and Selection: Iron Steels and High-Performance Alloys, ASM international, Materials Park OH. 1, (1993).

2 Hillenbrand H.G., Development and Production of High Strength Pipe line Steels, Niobium, Orlando Florida, 02-05 (2001).

3 Koval V.P., Khitarishviti M.G. and Osadtsiv P.S., Fiz. Khim. Mekh, Mater 10, (1974), p.113.

4 Test Method - Evaluation of pipeline steels for resistance to stepwise cracking, NACE Standard TM - 0284, (2003).

5 Testing of metal for resistance to SSC at ambient temperature, NACE Standard TM - 0177, (1996), p.367.

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 15, Preprint 40 submitted 9 October 2012

6 Robert Baboian., Corrosion tests and standards: application and interpretation, ASTM International 2nd edition, (2005).

7 Bai L. and Conway B.E., J. Electrochem. Soc. 138, (1991), p. 2897.

8 Bai L. and Conway B.E., Electrochem. Acta. 38, (1993), p.1803.

9 C. F. Barth and Steigerwald E. A. Met. and Mat. Trans. B. 1, 12 (1970), p. 3451.