Hydrogen Induced Cracking of API X52 and X60 Sour Service Steels Subjected to Pre-Strain under Prolonged H$_2$S Exposure

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Abstract. The effect of plastic deformation on API X52 and X60 sour service steels on hydrogen induced cracking was studied. Plastic deformation was performed with a tensile pre-strain with the percentage variation of strain. The HIC test was carried out with a duration of 168 hours of hydrogen charging to investigate the cracking behavior. After hydrogen charging, the cross sections of both steels were observed to find out hydrogen cracks. Ultrasonic testing was carried out on the specimen surface to see the distribution of laminated cracks. The hydrogen crack surface was observed using SEM. The results showed that the values of CSR, CLR and CTR increased with increasing percentage of pre-strain. Ultrasonic testing showed that the area influenced by HIC increased with increasing percentage of pre-strain. The susceptibility of API X52SS and X60SS to HIC increases with increasing percent of pre-strain. API Steel X52SS has better HIC resistance than X60SS on high pre-strain.

Keywords: hydrogen induced cracking, sour service, pre-strain, X52, X60

1. Introduction

Hydrogen Induced Cracking (HIC) is one of the most frequent problems in oil and gas pipelines when exposed to sour service environments containing hydrogen sulphide (H$_2$S) [1,2]. Steels exposed to sour environments absorb hydrogen atoms on their surface through H$_2$S corrosion reaction. The mechanism of the HIC begins with the diffusion of hydrogen atoms into the metal lattice. The hydrogen atoms then combine again to form hydrogen molecules. When reacting with water, H$_2$S can cause blistering failure, hydrogen embrittlement, hydrogen-induced cracking, sulfide stress cracking and so on. Such failure may decrease the lifetime of the pipeline.

In general, HIC is caused by three factors i.e. corrosive environment, stress components, and material susceptibility. Material susceptibility is influenced by many factors, including microstructure, presence of inclusion, and chemical composition [3-6]. Corrosive environments containing water and H$_2$S on oil and gas production are defined as sour services. The stress can be a residual stress that can come from strain during pipe making. The thickness of the plate
and the radius of the bending affect the magnitude of the strain received by the pipe during pipe manufacturing. In the smaller pipe diameter, the strain received will be greater [7-9].

There have been several studies that have been done to study the phenomenon of HIC on different types of alloys. For example Wan Keun Kim et al. [10] discusses the effect of metallurgical factors on HIC. Hitoshi Asahi et al. [11] describes the effect of the integration elements on HIC resistance. Mohtadi-Bonab et al. [12-16] has conducted extensive studies of HIC on steels. Several other studies were more concentrated on modification of microstructures and certain phases to improve HIC resistance. Until now, there are few references to discuss the effect of plastic deformation on HIC. Research on the effect of plastic strain on steel on HIC resistance is important because in pipeline manufacture, the steel plate undergoes plastic deformation. The strain generated by the plastic deformation can cause residual stress and may decrease its HIC resistance. The purpose of this study was to investigate the effect of plastic deformation on API X52 and X60 steels on HIC cracking under prolonged H<sub>2</sub>S exposure environment.

2. Materials and Methods

The steel used in this study was steel plate according to API 5L X52 and X60 specifications. The X52 steel used is specifically designed for sour-service conditions. Unlike the X52, X60 steel is not intended for the sour-service environment even though its chemical composition is still within the range for the sour-service design. X52 and X65 steels used respectively have a thickness of 6.3 and 14 mm. Table 1 shows the chemical composition of the two steels used in this study. The test specimens were taken from the HRC plate at ½ wide position. The position is selected to be a test specimen because there is more segregation and more susceptible to hydrogen-induced cracking (HIC) so it can be observed for the purposes of this study. The plate is then prepared into a tensile test specimen to be stretched using a tensile test machine. Strain applied is 4%; 8%; and 12%. Fig. 1 shows the specimen dimension for tensile pre-strain. The pre-strain gauge length section was then taken for HIC testing.

Table 1. Chemical composition of the steels (wt%)

|       | C    | Mn  | P    | S    | N    | Cu   | Mo   | Si   | Ni   |
|-------|------|-----|------|------|------|------|------|------|------|
| X52   | 0.039| 0.673| 0.0057| 0.0017| 0.037| 0.024| 0.003| 0.241| 0.167|
| X60   | 0.056| 1.008| 0.008 | 0.002 | 0.026 | 0.019 | 0.006 | 0.222 | 0.219 |

|       | Cr   | V    | Ti   | Nb   | Al   | B    | Co   | As   | Fe   |
|-------|------|------|------|------|------|------|------|------|------|
| X52   | 0.01 | 0.001| 0.002| 0.032| 0.044| 0.001| 0.025| 0.025| Bal.  |
| X60   | 0.114| 0.001| 0.003| 0.046| 0.035| 0.005| 0.044| 0.022| Bal.  |

Fig. 1. Specimen dimension for tensile pre-strain (in mm). The pre-strain gauge length section was then taken for HIC testing.
Samples without strain are also prepared as a comparison. The specimens that have been pre-strained were observed for their microstructure. Hardness and tensile testing are also performed on pre-strained specimens. Meanwhile, other pre-strained samples were also prepared for hydrogen induced cracking testing. Tensile tests were carried out following the ASTM E-8 standard [17]. Hardness testing was performed using Vickers microhardness with a load of 300 grams with a 15-second indentation period. The steel plate hardness was tested for as-received material, after pre-strained, and after HIC testing. Measurements of hardness values were performed in the longitudinal direction and on the thickness of the plate.

Observations using optical microscope were also performed to see the presence of inclusions before HIC testing and cracks that emerged after HIC testing. The specimens were transversally cut. The observations were performed on the short-transverse side to see the distribution of cracks and cross sections of the cracks. The length and thickness of the crack is then measured using a scale on an optical microscope. The observed cracks were then calculated to the values of the crack ratio.

Ultrasonic testing (UT) is performed before and after HIC testing. The purpose of UT testing prior to HIC is to identify the cleanliness of the steel. If a laminate or other defect is found, the plates in that section will not be used for HIC testing. After HIC testing, UT is reestablished to determine the crack distribution area inside the steel plate. The crack may be a laminate inside the test specimen. The crack area was then reconstructed to show the severity of the hydrogen damage to the steel plate.

Fig. 2 shows schematic diagram of HIC test. The test generally follows the NACE TM0284-2003 standard [18]. However, the standard followed was for manual preparation of test solutions, preparation of test specimens, and computation of crack comparisons. The duration of the test is set to exceed the standard duration of 96 hours. This study used a duration of 168 hours (7 days) so that cracks could be identified significantly for research purposes. Testing is done twice for each variation.

According to NACE standards, HIC test is done on pipes or vessels. However, in the present test, the specimen used is a stretched steel plate as a simulation of the actual strain experienced by the plate during the piping and installation process. The dimensions of the test specimens follow a predetermined standard with a size of 100 ± 1 mm and a width of 20 ± 1 mm. The specimens were then ground using abrasive paper with grit 320, rinsed with ethanol to remove the oil, dried, and then stored in the desiccators. The specimen should be used in less than 24 hours to avoid further contamination before it is inserted into the HIC test container.
The test solution used was solution A according to NACE TM0284-2003 standard [18]. The solution should contain 5% by weight of NaCl and 0.5% by weight of CH₃COOH dissolved in distilled water. Initial pH should be 2.7 ± 0.1. All the reagents added in the preparation of the test solution have a threshold of approximately 1 percent of each set value. The test is carried out at a temperature of 25 ± 3 °C. This solution is then purified (purging) using nitrogen gas for a minimum of 1 (one) hour at a flow rate of 100 mL per minute per liter of test solution. After purging has finished, the solution is saturated using H₂S gas at a flow rate of 200 mL per minute per liter of test solution for the first 60 minutes. Furthermore, H₂S is sufficiently bubbled at a lower flow rate (100 mL per minute) to maintain the acidity value of the solution in the pH range of 2.7 - 4.0. The pH measurements were repeated after the solution was finished saturated using H₂S. The specimen cross-section which has been tested by HIC is observed with an optical microscope to show hydrogen cracking. Fig. 3a shows the test specimens and crack dimensions to be used in calculating CLR, CTR, and CSR at the cross section. While Fig. 3b shows the location of UT testing on the surface of the specimen. The marked areas show examples of cracked areas identified by UT. The value of crack sensitivity ratio (CSR), crack length ratio (CLR), and crack thickness ratio (CTR) are calculated according to Eqs. (1) - (3) as follows [18]:

\[
CSR = \frac{\sum (a \times b)}{(W \times T)} \times 100% 
\]

\[
CLR = \frac{\sum a}{W} \times 100% 
\]

\[
CTR = \frac{\sum b}{T} \times 100% 
\]

where \(a\) is the cracking length, \(b\) represents the crack thickness, \(W\) is the specimen width, \(T\) is the specimen thickness.

The crack surface due to HIC was observed using Scanning Electron Microscope (SEM). Crack surfaces were observed by opening an existing crack after being exposed to liquid nitrogen. The observation was conducted on X60 specimen subjected to a plastic strain of 12% and has been exposed to the HIC test solution for 168 hours.

3. Results and Discussion

3.1. Effect of Plastic Strain on Microstructure and Mechanical Properties

Pre-strain causes the grains to be elongated in the direction of tensile loading. Fig. 4a to 4d respectively show the observed microstructure for 0% pre-strained X52, 12% pre-strained X52, 0% pre-strained X60 and 12% pre-strained X60. While Fig.5 shows the relationship between the change in the mean length of the grain measured in the direction of the tensile load by the variation of the pre-strain percentage for the studied steels.

Fig. 6 shows the relationship between strain and strength values for API X52 and X60, which have subjected to pre-strain. Meanwhile, Fig. 7 shows the relationship between strain with hardness for both steels after pre-strain. Figs. 6 and 7 show that for API X52 and X60 steels, the greater the percentage of pre-strain applied, the more strength and hardness of the two steels.
A hardness increase of approximately 5% was observed for each steel having a 4% increase in strain. The increase in strength and hardness due to the application of plastic deformation is called strain hardening, which is commonly observed in metal alloys.

Fig. 3. (a) Test specimens and crack dimensions to be used in calculating CLR, CTR, and CSR at the cross-section [18], (b) testing the UT on the surface of the specimen. The marked areas show examples of cracked areas identified by UT.

Fig. 4. Microstructure observation of the investigated steels (a) 0% pre-strained X52, (b) 12% pre-strained X52, (c) 0% pre-strained X60 and (d) 12% pre-strained X60.
Fig. 5. Relationship between the change in the mean length of the grain measured in the direction of the tensile load by the variation of the pre-strain percentage for the studied steels.

Fig. 6. Relationship between pre-strain and strength for X52 and X60 steels.
Fig. 7. Relationship between strain and hardness for X52 and X60 after pre-strain

3.2. Observation of Cracks and Fracture Surface

Figs. 8 and 9 show a crack observation on the cross-section of steel plate X52 and X60. In both images it is seen that both of the steel have cracks that occur due to exposure to hydrogen. In the figure also seen that the crack lengthwise in the direction of rolling. Steel that experienced a larger percentage of pre-tension strain exhibited a longer crack size. At the same OM observation scale, X52 steels with low yield strength exhibit a wider crack gap and clearer visible cracks compared to X62 steels. Fig. 9 shows that for X60 steel the HIC cracks propagated by stepwise manner.

Prior to the HIC test, a metallographic examination of the X52 and X60 steel plates was performed. The inclusions were found in X60 steel as shown in Fig. 10a. Through EDS testing it is known that the inclusion is manganese sulphide. Meanwhile, inclusion is not found in X52 steel. Considering its chemical composition, X60 steels are more likely to form more inclusions than X52 steels. All HIC cracks are known to initiate from inclusion and precipitate, and propagate in the direction of rolling [12,13,19,20].

In X52 steel the step-wise crack was not observed. This is because X52 steel has a better level of steel cleanliness. It should be noted that the occurrence of step-wise cracking is also influenced by the non-metallic inclusion distribution in alloys [21]. If inclusion is not distributed or even too small in the alloy, step-wise crack is not formed.

Cracks in X52 steel after the HIC test were found in the half-thickness of the plates. The area is where the occurrence of segregation. The segregation region is the most preferred area for hydrogen in the steel. Fig. 10b shows the location of segregation in X52 steel. The hard phase accumulates in the center of the steel plate during hot rolled steel making. Due to melting point differences, some elements forming hard phases are rejected into the center of the cross section.
of the steel plate. HIC crack propagates through the hard phase in these steels that are mostly located in the central part of the pipe plate [13,15,22-24]. In the area, the accumulation of inclusions causes a decrease in fracture toughness and makes the area very susceptible to HIC. The empty space between the inclusions and the metal matrix provides an atmosphere suitable for the concentration of hydrogen atoms thus making nucleation of the HIC crack [14].

![Fig. 8. Observation of cracks in cross-section of steel plate X52 after HIC test for (a) 4% pre-strain, (b) 8% pre-strain, (c) 12% pre-strain](image)

![Fig. 9. Observation of cracks in cross-section of steel plate X60 after HIC test for (a) 4% pre-strain, (b) 8% pre-strain, (c) 12% pre-strain](image)

Fig. 11 shows the fracture surfaces observed for X60 specimens after having 12% pre-strain and exposure on H2S for 168 hours. Planar cracks were opened for observation purposes. It appears that the fracture mode is transgranular brittle. HIC cracks propagate dominantly in transgranular manner [14]. In the picture also appears the presence of secondary cracks.
Fig. 10. The microstructure was observed on ½ thick of (a) steel X60 and (b) steel X52. The arrows indicate the presence of inclusions and segregation in steel X60 and X52, respectively.

Fig. 11. Fracture surface observation for X60 specimen after subjected to 12% pre-stain and HIC testing for 168 hours

3.3. Parameters and Distribution of HIC Cracks

All HIC parameters including CLR, CTR and CSR for both X52 and X60 steels that have undergone plastic strain were observed. Observation of distribution of cracked areas formed was also conducted to provide further information HIC susceptibility of both the steels. Fig. 12 shows the relationship between pre-strain and crack ratio (CLR and CTR) for X52 and X60 steels. From the figure it is seen that the value of CLR for steel X60 is higher than X52 steel for all variations of pre-strain. Nevertheless, the CTR values of the two steels are relatively similar, and do not experience significant changes with the increased application of pre-strain variations. This suggests that cracks tend to elongate with increasing pre-strain. Meanwhile, as shown in Fig. 13, CSR for both steels has the same tendency as CLR. Steel X60 has a higher susceptibility to HIC than X52. The CSR of both steels increases with increasing pre-strain. Susceptibility to HIC is believed to be strongly associated with increased strength and hardness, especially for X60 steels that have experienced significant strength and hardness after pre-strain.
Fig. 12. Relationship between pre-strain and crack ratio (CLR and CTR) for X52 and X60

Fig. 13. Relationship between pre-strain and CSR for X52 and X60
Mohtadi-Monah et al. [16] comparing the HIC parameters on the X70 and X60 found that the X70 is more susceptible to HIC. Cracks propagate across deformed grains, as observed using EBSD mapping [14]. Grains with high stored energy levels are more susceptible to HIC cracking. In steels with higher pre-strain levels, stored energy is also higher and causes cracks to form easily and propagate in the plastically deformed steel.

The distribution of cracked HIC areas examined using the UT from the surface of the specimen also exhibits a similar trend. Figs. 14 and 15 show the results of the reconstruction of cracked areas resulting from observations using the UT method. Areas containing cracks are represented by shaded areas. Two specimens were tested for each pre-strain variation. In the figures it is seen that for non-pre-strained (0% pre-strain) steels, the crack areas in both X52 and X60 are identified. It is seen that the crack area in X60 steel is wider than X52 steel. It should be noted again that this test was carried out with H2S exposure times that passed the general test standard, which is 168 hours.

Fig. 14. The observed laminate crack area from the upper side of X52 plate after HIC test for (a) 0% pre-strain, (b & c) 4% strain, (d & e) 8% strain and (f & g) 12% strain

Fig. 15. The observed laminate crack area from the upper side of X60 plate after HIC test for (a & b) 0% pre-strain, (c & d) 4% strain, (e & f) 8% strain and (g & h) 12% strain
The relationship between pre-strain and crack distribution area for X52 and X60 steels is shown in Fig. 16. In the figure it is clear that the increase in crack distribution area for X60 steels increases sharply compared to X52 steel. The presence of inclusions and increased hardness for X60 steels contributes and combines in increasing susceptibility to HIC cracking.

![Graph showing the relationship between pre-strain and crack distribution area for X52 and X60 steels.](image)

Fig. 16. Relationship between pre-strain and crack distribution area for X52 and X60 steels

4. Conclusions

Based on results from the investigation of hydrogen induced cracking of API X52 and X60 sour service steels subjected to pre-strain under prolonged H2S exposure, the following conclusion were drawn. Yield strength, tensile strength and hardness of the investigated steels increased with increasing tensile pre-strain. The observed HIC crack propagates in the direction of rolling. The segregation region is the most preferred area for HIC cracking in the X52 steel, while in X60 steel where inclusions were found, the HIC cracks initiate on the inclusions. HIC cracks propagate in transgranular manner. The value of CLR for steel X60 is higher than X52 steel for all variations of pre-strain. The CTR values of the two steels are relatively similar, and do not change significantly with pre-strain variations. Cracks tend to elongate with increasing pre-strain. Steel X60 has a higher susceptibility to HIC than X52. The CSR and crack distribution area of both steels increases with increasing pre-strain. Susceptibility to HIC is associated with an increase in strength and hardness after tensile pre-strain.

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6. References
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