Effect of tempered martensite micro structure on strength and SSC resistance of the HSLA steel with varying carbon content

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Abstract:

The effect of microstructure of high strength low alloy steel (HSLA) on strength and sulfide stress cracking (SSC) resistance is investigated for achieving superior sour resistance to the existing sour grade materials. Modified AISI 4130 (1.0wt%Cr-0.7wt%Mo-0.1wt%V) steel with varying carbon content from 0.15wt% to 0.58wt% quenched and tempered were analyzed with respect to martensite sub-structure (such as block size), precipitation of carbide, dislocation density and hydrogen absorption behavior. By increasing carbon content, the sizes of martensite blocks were refined (become smaller). It resulted in increasing strength of the steel even after high temperature tempering. The high temperature tempering led to reducing dislocation density and spheroidizing carbides. Hydrogen absorption in the steel with higher carbon content was reduced in a sour environment due to the reduction in dislocation density.

SSC resistance was evaluated using tensile tests according to NACE Standard TM0177 Method A. The steel with higher carbon content had higher threshold strength of SSC resistance, which is likely to be due to the above mentioned microstructural improvements.

Keywords: Low-alloy-steel, dislocation density, hydrogen diffusivity, sulphide stress cracking
1 Introduction

The need for higher strength steels has become more apparent with the increasing energy demands and the consequential increasing development of high pressure high temperature oil and gas fields. However, it is well known that high strength steels suffer from Sulfide Stress Cracking (SSC) in sour environments. It is generally accepted that SSC is a form of hydrogen embrittlement cracking, caused by absorbed atomic hydrogen into steels. The role of H$_2$S is thought to be a poison, accelerating hydrogen absorption into steels. For that reason, it has been necessary to develop special materials with sufficient resistance to SSC for high strength OCTG used in sour environments. Numerous fundamental studies have been conducted on how to improve SSC resistance. It is well known that microstructural modifications strongly affect SSC properties. In particular, it is widely recognized that a tempered martensitic microstructure produced by quenching and tempering heat treatments is a preferred microstructure [1]. A microstructure with fine prior austenite grains is considered the optimum structure to prevent intergranular cracking [2, 3]. Niobium addition to steels is effective in the microstructural refinement [2]. Based on the above microstructural modifications, 1%Cr-0.7%~0.9%Mo-Nb steels have been developed for the 110ksi (specified minimum yield strength of 758MPa) grade for sour service [4-5]. Additionally, a combination of lower dislocation obtained by high temperature tempering and precipitation hardening is realized to be a desirable structure for higher strength mild sour application [6-8]. Currently, detail metallurgical analysis have been conducted from the view point of martensite substructure [9] and dislocation density [10]. However, there are not many researches that deal with effects of alloying element on these microstructures and properties for application as SSC resistant high strength low alloy steel. In particular, the effect of carbon which is one of the most effective element in strengthening low alloy steel has not been clarified.

This paper describes the effects of carbon content in low alloy steel on mechanical property and SSC resistance. A mechanism of the effects for carbon is discussed from the viewpoints of hydrogen diffusivity, hydrogen absorption and microstructure.

2 Experimental

2.1 Material

Modified AISI4130 steels (1.0wt%Cr-0.7wt%Mo-0.1wt%V) of laboratory-melting with different carbon content were prepared. They were melted in a vacuum furnace and cast into 50kg ingots. The ingots were hot rolled into plates with 15mm thickness and then the plates cooled in air to room temperature. The plates were reheated to temperatures above Ac3 temperature for quenching. During the hot rolling and the heat treatment, the temperature and the holding time were controlled to obtain the prior austenite grain diameter in the range of 10 to 20 micro meters. Cooling devices used for quenching were a water bath for the 0.15-0.40%C steels and an oil bath for the 0.46%C or higher carbon steels. Hardness(HRC) of the only quenched plates of all the steels were satisfied with the API 5CT criterion for 90% of martensite. The quenched steel plates were tempered (QT) at several temperatures to control strength levels. Holding time was approximately 60min for each of tempering temperature.

The steels listed in Table 1 were used for investigation of influences of tempering temperature on mechanical property, dislocation density, hydrogen diffusivity and absorption. In order to evaluate SSC resistance of higher carbon steel, an extra melt was prepared. Chemical composition of the steel is listed in Table 2.
Table 1: Chemical compositions of the test steels (wt %)

<table>
<thead>
<tr>
<th>Mark</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Mo</th>
<th>V</th>
<th>others</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15%C</td>
<td>0.15</td>
<td>0.29</td>
<td>0.38</td>
<td>1.01</td>
<td>0.70</td>
<td>0.10</td>
<td>Microalloys (Ti, Nb)</td>
<td>balance</td>
</tr>
<tr>
<td>0.26%C</td>
<td>0.26</td>
<td>0.29</td>
<td>0.40</td>
<td>1.01</td>
<td>0.71</td>
<td>0.10</td>
<td>Inpurities (P,S,N,O)</td>
<td>balance</td>
</tr>
<tr>
<td>0.31%C</td>
<td>0.31</td>
<td>0.28</td>
<td>0.43</td>
<td>1.04</td>
<td>0.70</td>
<td>0.10</td>
<td></td>
<td>balance</td>
</tr>
<tr>
<td>0.50%C</td>
<td>0.50</td>
<td>0.29</td>
<td>0.39</td>
<td>0.99</td>
<td>0.70</td>
<td>0.10</td>
<td></td>
<td>balance</td>
</tr>
<tr>
<td>0.58%C</td>
<td>0.58</td>
<td>0.30</td>
<td>0.40</td>
<td>1.03</td>
<td>0.73</td>
<td>0.10</td>
<td></td>
<td>balance</td>
</tr>
</tbody>
</table>

Table 2: Chemical composition of the test steel for SSC resistance testing (wt %)

<table>
<thead>
<tr>
<th>Mark</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Mo</th>
<th>V</th>
<th>others</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.51%C</td>
<td>0.51</td>
<td>0.20</td>
<td>0.44</td>
<td>0.99</td>
<td>0.71</td>
<td>0.10</td>
<td>Microalloys (Ti, Nb)</td>
<td>balance</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Inpurities (P,S,N,O)</td>
<td></td>
</tr>
</tbody>
</table>

2.1 Tensile testing
Yield strength (0.2% proof strength) of the steel was measured by tensile testing using a round bar specimen with a diameter of 6mm and a gauge length of 30mm subjected from the longitudinal direction in the middle of the QT steel plate thickness.

2.2 Measurement of dislocation density
Dislocation density of the QT plate was measured using X-ray diffraction analysis of peak broadening (extracting full width at half maximum, FWHM), using Co-Kα radiation. The FWHM was corrected by using a FWHM of annealed pure Fe. For the X-ray diffraction analysis, the diffraction profiles of αFe(110), (211) and (222) reflections were measured. The dislocation density, ρ, was estimated from the equation [11] (1), where b is the burgers vector (0.25 nm) and ε is the local strain obtained by Williamson–Hall method [12].

$$\rho = 14.4 \frac{\varepsilon^2}{b^2}$$  \hspace{1cm} (1)

It is well known that the dislocation density value estimated by this Williamson-Hall method is somewhat higher value than the value obtained by the modified Warren–Averbach (MWA) method [13, 14]. However, in case of high temperature tempered martensite, the difference between both of the values could not be significant [15]. The sample for the XRD analysis was cut into a proper size (20mm x 20mm x 3mm) from the mid-portion of the QT steel plate and polished mechanically with emery papers down to No. 600, followed by electropolishing which performed to remove the extra dislocations introduced by mechanical polishing. The electropolishing was carried out using a 1M HClO₄ acetic acid solution with a voltage of 27 V to remove approximately 50 μm of material from the surface of the sample.

2.3 Measurement of hydrogen diffusion coefficient
Absorbed hydrogen content is considered to be a factor that determines hydrogen embrittlement. In general, absorbed hydrogen content is inversely proportional to hydrogen diffusion coefficient. A hydrogen permeation testing was carried out in order to measure hydrogen diffusion coefficient in the QT steel by means of an electrochemical method [16]. The specimen for the hydrogen permeation testing was prepared as follow. A sample with 30mm in diameter and 1.5mm in thickness was machined from the mid-thickness of the QT steel plate. The sample was mechanically polished by 1200 grid emery paper. Finally, the sample was chemically polished by immersing into HClO₄ acetic acid solution. Before the hydrogen permeation testing, the exit side of the specimen surface was nickel coated. The specimen with the circular area of 3.46cm² was mounted between the cells. The exit cell was filled with 0.1M NaOH solution, while the hydrogen charging cell was filled with 0.5M NaCl+3g/l NH₄SCN as a hydrogen recombination poison. The temperature of each cell was
25°C. The exit side of specimen was polarized 0V vs. saturated calomel electrode (SCE), while the hydrogen charging side of specimen was polarized from -0.9V to -1.2V vs. SCE. Through the experiment, hydrogen atoms that permeate the membrane from the hydrogen charging side were oxidized to hydrogen ions on the inner surface. Hydrogen oxidizing current density \( J \) (A/cm\(^2\)) measured by a potentiostat gives hydrogen permeation coefficient \( J_L \) (A/cm), where \( L \) is the thickness of the specimen (approximately 0.15cm). The hydrogen diffusion coefficient \( D \) using the half-rise time \( t_{1/2} \) formula was derivated by the equation (2), where \( t_{1/2} \) is time needed to obtain one-half of the steady state current \( J_{\text{max}} \).

\[
D = \frac{0.14L^2}{t_{1/2}} \quad (2)
\]

2.4 Hydrogen absorption behaviour
The immersion test was conducted using duplicate coupon specimen with 2mm thickness, 20mm width and 20mm length for hydrogen absorption measurement. The surfaces of the test pieces was ground to a 600 grid emery paper and degreased prior to immersion test. The test solution of the immersion test was 5.0 wt% NaCl and 0.5 wt% CH\(_3\)COOH solution with 0.1 MPa H\(_2\)S specified as solution A in NACE TM0177. The test duration was 168 h. After the immersion, the specimen was rinsed with deionized water and ethanol, and ensured drying to prevent rust formation on the specimens following a hydrogen measurement. The specimen was placed inside of a refrigerator at -50°C just after the end of the immersion to prevent hydrogen release. A piece with 10 mm length was cut using a grinding cutter with the circulation of coolant at -40°C, the corrosion products removed and cleaned prior to the hydrogen analysis. The absorbed hydrogen content in the cut sample was measured by Thermal Desorption Analysis (TDA). Then the specimen was heated up at a heating rate of 10°C/min. Degassed hydrogen from the sample was detected by the quadrupole mass spectroscopy. Absorbed hydrogen content in the specimen was derived by integrating the hydrogen evolution rate in the first peak by 350°C.

2.5 SSC resistance testing
The susceptibility to SSC was evaluated using uniaxial constant load test (proof ring test), generally in accordance with NACE TM 0177-2005 Method A. The tensile specimen with a gauge section of 6.35mm diameter and 25.4mm length was subjected from the longitudinal direction in the middle of the QT steel plate thickness. The specimen was immersed in test solution and stressed via uniaxial tension. The applied stress was 90% of actual yield strength and the test duration was 720 hours. The test solution was the solution A with 0.1MPa H\(_2\)S saturated at 24°C.

3 Results
3.1 Tempering curve
Effects of tempering temperature in the range from 640°C to 720°C on strength in the 0.15%C, 0.26%C, 0.50%C and 0.58%C steel are shown in Fig. 1. The yield strength and ultimate tensile strength decreased with the increase in tempering temperature. However, the carbon content of steel also affected strength. The yield strength and ultimate tensile strength increased with the increase in the carbon content in steel at each tempering temperature. At the tempering temperature of 680°C, the yield strength of the 0.15%C steel, the 0.26%C steel and the 0.50%C steel were 846MPa, 935MPa and 1025MPa, respectively. Therefore, further high strength can be achieved even at high tempering temperature by using the high carbon steel.
It is known that the decrease in yield strength with increasing tempering temperature was related to decrease in dislocation density. Fig.2 shows the effect of tempering temperature on the dislocation density estimated by the X-ray analysis for the 0.15% C, 0.26% C, 0.50% C and 0.58% C steel. The dislocation density decreased with increasing tempering temperature in any of these steels. It is interesting to note that the dislocation density of the high carbon steel was lower compared with that of low carbon steel in the tempering temperature range. Fig.3 shows the relationship between the dislocation density and yield strength. As can be seen in Fig. 3, high carbon steel has higher yield strength than low carbon steel even with same dislocation density.

3.3 Hydrogen diffusion coefficient
Hydrogen diffusion coefficients estimated by the hydrogen permeation test results are summarized in Table 3. Fig.4 shows the effect of the dislocation density on the hydrogen diffusion coefficient in 0.26% C steel and 0.50% C steel. In this data, the hydrogen diffusion coefficient became higher with decreasing the dislocation density by increasing tempering temperature. Regarding the yield strength, the hydrogen diffusion coefficient in the 0.5% C steel was higher than that of 0.26% C steel with same yield strength levels (as seen in Fig. 5).
### Table 3  Summary of hydrogen diffusion coefficient measured.

<table>
<thead>
<tr>
<th>Steel</th>
<th>Tempering Temperature</th>
<th>Yield strength</th>
<th>Hydrogen Diffusion Coefficient (D) build up</th>
<th>Hydrogen Diffusion Coefficient (D) decay</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.26%C</td>
<td>660°C</td>
<td>1057 MPa</td>
<td>0.69 x10^6 cm/s</td>
<td>0.71 x10^6 cm/s</td>
</tr>
<tr>
<td></td>
<td>680°C</td>
<td>935 MPa</td>
<td>1.2 x10^6 cm/s</td>
<td>1.2 x10^6 cm/s</td>
</tr>
<tr>
<td></td>
<td>720°C</td>
<td>760 MPa</td>
<td>2.9 x10^5 cm/s</td>
<td>2.7 x10^5 cm/s</td>
</tr>
<tr>
<td>0.50%C</td>
<td>680°C</td>
<td>1025 MPa</td>
<td>1.3 x10^6 cm/s</td>
<td>1.3 x10^6 cm/s</td>
</tr>
<tr>
<td></td>
<td>720°C</td>
<td>830 MPa</td>
<td>4.1 x10^5 cm/s</td>
<td>3.1 x10^5 cm/s</td>
</tr>
</tbody>
</table>

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### 3.4 Hydrogen absorption behaviour

Fig. 6 shows the relationship between yield strength and absorbed hydrogen content in steel after immersed in the solution A with saturated 0.1MPa H₂S for 168hrs. The absorbed hydrogen content tends to increase with increasing yield strength. However, the absorbed hydrogen content of higher carbon steel was lower than that of low carbon steel. It is likely that absorbed hydrogen content is reduced due to low dislocation density in high carbon steel also high strength with treated high temperature tempering.
3.5 SSC resistance testing
SSC resistance testing was conducted for the 0.51%C steel with varying yield strength by changing the tempering temperature. Fig. 7 summarizes the SSC test results. The steel had good SSC resistance up to the 880MPa of yield strength which is higher than the upper limit of API C110 grade (828MPa).

Fig. 7: Relationship between yield strength and time-to-failure of NACE-TM0177 method A (0.1MPa H2S, solution A, applied stress of 90% actual YS)

4 Discussion
4.1 Effect of dislocation density on hydrogen diffusion coefficient of tempered martensite
As shown in Fig. 4, the hydrogen diffusion coefficients were almost inversely proportional with the dislocation densities regardless of the carbon contents in the steels. The effective hydrogen diffusivity, D in a material with reversible traps are expressed in the Oriani's equation [17] (3), where $D_L$ is the hydrogen diffusion coefficient in lattice site, $N_t$ is the number of the trap sites per unit volume, $N_L$ is the number of the lattice sites per unit volume, $E_b$ is the binding energy of the trap site, R is the gas constant, T is the temperature.

$$D = \frac{D_L}{1 + N_t/N_L \times \exp (E_b/RT)} \quad (3)$$

$N_t/N_L$ is expressed in the equation (4) by converting the equation (3).

$$\frac{N_t}{N_L} = \left(\frac{D_L}{D} - 1\right) \times \frac{1}{\exp (E_b/RT)} \quad (4)$$

It is possible to evaluate $N_t$ by using the equation (4) with D measured in this study, $N_L = 5.1 \times 10^{29} \text{ m}^{-3}$ [18], $D_L = 8.3 \times 10^{-9} \text{ m}^2/\text{s}$ [19], $E_b = 27\text{kJ/mol}$ [19], R is 8.314 J/mol, and T is 298K. The estimated $N_t$ values are between from $2 \times 10^{26}$ to $1 \times 10^{27} \text{ m}^{-3}$, which are similar to the value for cold rolled iron reported previously [20, 21]. It could be suggested from these comparison that the hydrogen diffusion coefficient measured in this study was strongly affected by the dislocation which act as trap sites.
Effect of carbon content in steel on sub structure of tempered martensite

As mentioned above, high carbon steel applied the high temperature tempering tends to have high strength, low dislocation density, and high hydrogen diffusivity. These characteristics are discussed from a view point of microstructure of the tempered martensite.

Fig. 9 shows inverse pole figure and high angle boundary map (misorientation angle $\geq 15$ degree) provided by using a Electron BackScattering Diffraction (EBSD) analysis for the 0.15%C steel, the 0.31%C steel and the 0.51%C steel tempered at 700°C. All of these inverse pole figures indicate tempered lath martensite, however, size of sub-structure are different. A grain of sub-structure is defined as a block of pixels enclosed by the boundaries. A diameter of the grain can be estimated from the area of the grain. Fig. 10 shows distribution of the grain diameter which were obtained from Fig. 9(d, e and f). As can be seen in Fig. 10, the grain became smaller with increasing the carbon content of the steel. A mode of grain diameter is below 1.5$\mu$m estimated from Fig. 9 for the 0.51%C steel. As previous study in Fe-C alloy [22], sub-structures (such as packet and block sizes in lath martensite) decrease with an increase in carbon content because of a lowering transformation temperature (martensite start temperature, Ms). In the present study, the prior austenite grain size was similar in all the steels, and the cooling rate was sufficient during the quenching, while the Ms obtained by dilatometer were 420°C for the 0.15%C steel, 380°C for the 0.31%C, and 280°C for the 0.51%C steel. Therefore the tendency of the grain refinement is caused by the lowering Ms due to increase in carbon content.

Material's strength is expected to increase in a manner described by the well-known Hall-Petch relationship. Similarly, in the present study, it is probably that the high carbon steel had higher strength due to maintained smaller microstructure in spite of low dislocation density after the high temperature tempering.

As shown in Fig. 7, High carbon steel has a good SSC resistance with high strength. This reason for this are that the main mechanism of strengthening is grain refinement which does not rely on dislocation hardening, and the lowering dislocation density by high temperature tempering provide reduction of hydrogen absorption and/or high hydrogen diffusivity.
Fig. 9: Invers pole figure of the 700°C tempered 0.15%C steel (a), the 0.31%C steel (b), the 0.51%C steel (c) and grain boundary map (d), (e), (f) in same field of (a), (b), (c) respectibily.
5 Conclusion

Effect of carbon content in 1%Cr-0.7%Mo-0.1%V steel with tempered martensite microstructure on mechanical property, dislocation density, hydrogen diffusivity, and SSC resistance was investigated by a laboratory heat treatment experiment with changing tempering temperature. The results are as follows.

(1) Dislocation density in the tempered martensite was decreased with increasing the carbon content from 0.15% to 0.58% even if they had same strength, mainly because of increasing tempering temperature.

(2) Hydrogen diffusion coefficient increased with decreasing the dislocation density. In the same yield strength level between 830MPa to 1025MPa of the steels, The hydrogen diffusion coefficients of 0.5%C-1%Cr-0.7%Mo-0.1%V steel was higher than that in 0.26%C-1%Cr-0.7%Mo-0.1%V steel.

(3) Absorbed hydrogen content in high carbon steel when immersed in NACE-solution A saturated 0.1MPa H₂S was lower than that in low carbon steel. This is likely due to the lower dislocation density in high carbon steel that was tempered at higher temperature.

(4) 0.51%C-1%Cr-0.7%Mo-0.1%V steel had higher limit yield strength over API C110 grade for SSC prevention, which was confirmed by NACE-TM0177 Method A with the condition of the NACE solution A saturated with 0.1MPa H₂S.

(5) Very fine sub-structure (grain size below 1.5μm) of tempered martensite of the higher carbon steel probably also contributed to high strength and improved SSC resistance.

A good combination of high strength and SSC resistance are achieved by using higher carbon steel applied high temperature tempering. It can be expected that this knowledge contribute to develop an ultra high strength casing grade for application in sour environment. For this purpose, it is necessary to determine applicable environment (pH-pH₂S) for each strength levels.

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References