Influence of Heat Treatment on the Corrosion of Carbon Steel in Environment Containing Carbon Dioxide and Acetic Acid

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ABSTRACT. Experimental investigations were carried out to study the influence of heat treatment on the corrosion behaviour of API 5L X65 pipeline steel in the presence of acetic acid HAc and carbon dioxide CO2 environment. CO2 corrosion has been recognized as one of corrosion threats resulting in a loss of pipeline integrity. In this work, the specimens taken from the X65 steel pipe were subjected to respective heat treatment which was annealing, normalizing and quenching. As-received specimens were included as control. CO2 corrosion experiments using three-electrode glass cell system were performed with and without acetic acid. Corrosion rates were measured by means of weight loss and Linear Polarization Resistance (LPR) electrochemical methods. Results showed that heat treatments were found to affect the corrosion rates. Annealed specimen showed the lowest corrosion rate while quenched specimen appeared to corrode more compared to other specimens. The presence of acetic acid in aqueous CO2 environment generally aggravated the corrosion rate for all heat-treated specimens.

1. Introduction

The structural integrity of transportation pipelines is of paramount importance in the oil and gas industries. Carbon steel remains the preferred choice of pipeline material because it is economical, durable and adequate in strength¹. Depending on the specific applications of the carbon steel components, different forms of heat treatment process can be applied to alter the mechanical properties, such as the yield strength, tensile strength, hardness, impact resistance and ductility. Normalizing is typically applied to the pressure retaining components: seamless steel pipe, pipe fittings, shell for vessel, annealing heat treatment is applied to parts having uniform wall thickness, while quenching is applied to components subjected to high pressure service such as injection nozzle or high service temperature such as boiler. However, the carbon steel pipeline material is susceptible to internal corrosion when subjected to hydrocarbon products containing corrosive species such as CO2, H2S and/or organic acids.

Heat treatment is a process of heating and cooling metals to achieve desired physical and mechanical properties through the modification of the crystalline structure. Heating temperature, length of time and rate of cooling are some of the significant variables that could impact the properties of the heat-treated metals [1,2]. The common forms of heat treatment done to carbon steel are
annealing, normalizing and quenching. In annealing, the steels are held above the austenitic temperature and then slowly cooled in a furnace to produce coarse grain structure of pearlite with excess of ferrite or cementite. This results in annealed parts with uniform softness and stress relieved. In normalizing, the steels are heated until it passes the austenitic temperature and then air-cooled to produce refined grain structure. The normalized parts have improved hardness, strength and machinability. This heat treatment is more extensively used since it is more economical. In quenching, the steels are rapidly cooled in water or oil to produce needle-like martensitic structures [3]. It is apparent that the choice of heat treatment cycle and cooling path determine the final microstructure and properties of the steels. Generally, refined grain microstructure in normalizing yields to combined high strength and high ductility; however it tends to increase the difference in potential for galvanic action to occur, thereby leading to higher corrosion rate [3,4]. For instance, the impact strength is improved after heat treatment as a result of residual stress relief [5]. On the other hand, the corrosion and electrical properties can be slightly affected after the heat treatment.

CO2 corrosion is considered as sweet corrosion that commonly occurs internally in the transportation pipelines carrying hydrocarbon products. CO2 gas is often produced alongside with hydrocarbon phase, hence it is readily present in the produced fluids. Dry CO2 gas is not corrosive, but becomes corrosive when it dissolves in formation water to form carbonic acid (H2CO3):

\[
CO_2 + H_2O \leftrightarrow H_2CO_3
\]  

(1)

Carbonic acid is a weak acid that ionizes partially into bicarbonate (HCO3\(^{-}\)) ion and carbonate (CO3\(^{2-}\)) ion in two-step reactions \(^6\) shown in equation (2).

\[
H_2CO_3 \leftrightarrow H^+ + HCO_3^{-}
\]  

(2)

\[
HCO_3^{-} \leftrightarrow H^+ + CO_3^{2-}
\]  

(3)

The cathodic reactions are either from the proton hydrogen reduction in Eq. (4) through the buffering effect or the direct reduction of carbonic acid on the metal surface \([6,7]\) in Eq. (5).

\[
2H^+ + 2e^- \leftrightarrow H_2
\]  

(4)

\[
2H_2CO_3 + 2e^- \leftrightarrow H_2 + 2HCO_3^{-}
\]  

(5)

Organic acid is naturally present in the oil field brines. Acetic acid (HAc) appears to be the most common type of organic acid with concentrations ranging from hundreds to thousands of ppm. Field experience considered HAc to be a corrosion threat. A number of laboratory work have been performed on the role of HAc in CO2 corrosion over wide ranging test conditions as summarized in the literature review \([8,9]\). Some studies focused on the role of acetic acid in top of line corrosion (TLC) cases, which it accelerates the cathodic reaction and local corrosion rate \([10,11]\). Others researchers argued that HAc has a negligible effect on the overall corrosion rate, but seems to stimulate localized attack \([12]\). Similar to carbonic acid, acetic acid is a weak acid that dissociates partially in water into hydrogen ion and acetate ions:

\[
HAc \leftrightarrow H^+ + Ac^{-}
\]  

(6)

However, HAc is a stronger acid compared to carbonic acid (pKa 4.76 versus pKa 6.37 at 25°C). As such, it is generally accepted that HAc affects the cathodic reaction and aggravates the corrosion in CO2-containing media \([13,14]\). The main concern is the presence of free acetic species as a buffer which can dissociate partially to provide H\(^+\) source when needed in cathodic reaction \([8]\). The degree of HAc dissociation is governed by pKa, pH and temperature. The lower the pH, the more likely the HAc dissociates. The concentration of the free acetic species is given in the following mass conservation equation \([12]\):

\[
[HAc_{free]} = \frac{[HAc_{total}]}{(1 + K_a/[H^+]})
\]  

(7)

where \(K_a\) is the dissociation constant for HAc that varies with temperature.

Table 1 shows the calculated dissociation of acetic species at 25°C, pH 5.5, in which approximately 15% of total HAc is undissociated acetic species.
Table 1. Concentration of undissociated HAc and Ac⁻ at 25°C, pH 5.5

| Total Hac (PPM) | Undissociated Hac (PPM) | Acetate, Ac⁻ (PPM) |
|----------------|-------------------------|-------------------|
| 100            | 15                      | 83                |
| 500            | 76                      | 417               |
| 1,000          | 152                     | 834               |
| 1,500          | 228                     | 1251              |

As demonstrated by several related work [8,13], the self-dissociation of two weak acids in CO₂/HAc containing media can be more corrosive due to the buffering effect. The Fe²⁺ ions are formed based on the following two overall aqueous reactions:

\[ 2\text{HAc} + \text{Fe} \rightleftharpoons \text{Fe}^{2+} + 2\text{Ac}^- + \text{H}_2 \quad (8) \]
\[ 2\text{H}_2\text{CO}_3 + \text{Fe} \rightleftharpoons \text{Fe}^{2+} + 2\text{HCO}_3^- + \text{H}_2 \quad (9) \]

The charge balance equation for electroneutrality condition (10) of the bulk aqueous solution is expressed as:

\[ [\text{H}^+] + 2[\text{Fe}^{2+}] = [\text{OH}^-] + [\text{Ac}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] \quad (10) \]

2. Methodology

2.1. Materials

Eight (8) specimens were sectioned from a carbon steel pipe grade API 5L X65, with the chemical composition shown in Table 2. The specimens were classified into 4 groups: A, B, C and D with each group having two specimens. Group A was the as-received specimen as control. For annealing, group B specimens were furnace heated to 750°C, hold for 30 minutes and allowed to be cooled in the furnace for 24 hours. For annealing, group C specimens were furnace heated to 750°C, hold for 30 minutes and allowed to cool in still air to ambient temperature. In quenching, group D specimens were furnace heated to 750°C, hold for 30 minutes and quenched in water medium. After the heat treatment, the specimens were etched for surface examination using optical microscope. Corrosion experiments were performed by weight loss method and linear polarization resistance (LPR) method in a standard three-electrode glass cell set up. Prior the experiment, the exposed surfaces of the specimens were consecutively polished with silicon carbide sand paper up to 600 grit, rinsed in de-ionised water, cleaned in alcohol in an ultrasonic bath and finally air-dried with blower.

Table 2. Elemental composition (wt%) of API 5L X65 carbon steel

| Element | C | Mn | Si | Cr | Ni | Mo | Fe |
|---------|---|----|----|----|----|----|----|
| wt.%    | 0.13 | 1.25 | 0.35 | 0.12 | 0.08 | 0.16 | balance |

2.2. Test setup

Corrosion experiments were performed in a 1-litre glass cell using three-electrode system as shown in Figure 1. The electrodes comprise silver/silver chloride (Ag/AgCl) as the reference electrode (RE), stainless steel rod as the counter electrode (CE) and mounted sample as the working electrode (WE). The test solution was prepared from 3 wt.% sodium chloride (NaCl) dissolved in de-ionised water. Prior to the test, the solution was heated continuously with CO₂ gas for at least 45 minutes to remove the dissolved oxygen. The gas bubbling continued during the experiment to ensure wet CO₂ saturation and to maintain slight positive pressure over atmospheric. The solution pH was adjusted by adding HCl or NaOH.
2.3. Test Parameters

Table 3 shows the test parameters for the glass cell experiments. The test parameters were chosen so as to simulate the CO$_2$ corrosion in the presence of acetic acid encountered in flow lines. For comparison, the first set of tests was performed without acidic acid HAc in CO$_2$ environment at pH 5.5. For the second set of tests, HAc of 1000 ppm was added at the start of test to the solution and the solution pH is adjusted to pH 5.5. Linear polarization resistance (LPR) technique, as per ASTM G59 [15], was used to monitor the in-situ corrosion rate at every half hour throughout the 48-hour duration. In LPR, the working electrode was polarized at ±10 mV from the open circuit potential at a sweep rate of 0.125 mV/s. Weight loss by immersion technique as per ASTM G31 [16] is performed for 50 to 65 hours as a measure of general corrosion rate. The calculation for general corrosion rate is given as:

$$CR = \frac{\Delta m \times 24 \times 365 \times 10}{\rho \times A \times t}$$

(11)

where $\Delta m$ is mass loss (g), $\rho$ is density (g/cm$^3$), $A$ is exposed surface area (cm$^2$), and $t$ is exposure time (h).

| Element                     | Value                           |
|-----------------------------|---------------------------------|
| Steel sample                | API 5L x-65                     |
| Heat treatment              |                                 |
| Control                | Annealing                  | Normalizing                   | Quenching       |
| Test solution              | 3 wt% NaCl$_{aq}$, saturated with CO$_2$ |
| Solution pH                | 5.5                           |
| Temperature                | 25°C                          |
| Total HAc (ppm)            | 0, 1000                      |
| Measurement techniques     | Linear polarization resistance LPR : 48 h |
|                            | Weight loss : 50 to 65 h       |

3. Results and Discussion

3.1. Microscopy Analysis

The optical microstructure surface for four groups: (a) as-received control (b) annealed; (c) normalize; and (d) quenched specimens of X65 carbon steel are shown in Figure 2. With heat treatment applied, different microstructure surfaces were observed. Annealed specimen displayed a much coarse pearlite distribution. Normalized specimen showed shorter grains. For quenched sample, the needle shape morphology was identified as martensite structure.

Figure 1. Three electrode glass cell setup: (1) reference electrode, (2) working electrode, (3) counter electrode, (4) CO$_2$ gas inlet, (5) 3 wt.% NaCl aqueous solution.
Figure 2. Optical photomicrographs of (a) as-received; (b) annealed; (c) normalized; (d) quenched specimens (400 X).

3.2. Effect of Heat Treatment

Figure 3 shows the variations of LPR corrosion rate with time (48 hours) at pH 5.5 and 25°C for samples subjected to different types of heat treatments in saturated CO$_2$ environment without the presence of acetic acid. All LPR corrosion rates of the specimens showed increasing trend in the first 5 hours before it remained consistent throughout. For as-received control specimen, the corrosion trend was consistent with the final corrosion rate was 1.3 mm/yr. Upon comparison, the trend of corrosion rate for normalized specimen matched with the control specimen. This showed that the as-received control specimen was similar to the normalized steel. The quenched specimen showed the highest corrosion rate with the final corrosion rate at 1.7 mm/yr while the annealed steel specimen showed the lowest with a final corrosion rate of 1.0 mm/yr. Results showed that annealed specimen with coarser grain structure exhibited better corrosion resistance over other specimens. The findings were comparable to a similar study by Siedu [17], in which the bigger the grain structure the more corrosion resistant it was. This can be explained by larger grains tends to minimize the difference in potential for galvanic cell to occur [3,4].
3.3. Effect of Acetic Acid

Figure 4 shows the variation of LPR corrosion rates with time (48 hours) for baseline and different heat treated specimens in CO$_2$/HAc containing environment at pH 5.5 and 25°C. In such condition, the undissociated HAc is approximately 152 ppm or 15% of the total 1000 ppm HAc. LPR results show that the overall average corrosion rates for all specimens increase to about 2 mm/yr, except for the annealed specimen at about 1.5 mm/yr. The increment in average corrosion rates ranges from 30% to 55%. This can be explained by the presence of weak acetic acid that acts as a buffer source for hydrogen that contributes to additional cathodic reactions. Similar findings were also reported by others [8].

3.4. Weight Loss Results

In order to better capture the long term corrosion effect, weight lost (WL) specimen were submerged in the test fluids for more than 60–90 hours at 25°C in 3 wt% NaCl saturated with CO$_2$. Without the addition of HAc, the WL results in Figure 5 show that the corrosion rate of the quenched specimen
was the highest at 1.7 mm/y which agreed with the LPR results. The annealed sample had the lowest corrosion rate at 1 mm/y and was comparable to the LPR results. With the addition of 1000 ppm HAc, the WL corrosion rates for all specimens generally increased to about 2 mm/yr except for annealed steel specimen at 1.5 mm/y as shown in Figure 6. The results were in agreement with the LPR results [18]. Overall, the corrosion rates for all specimens were higher because of the addition of acetic acid at pH 5.5 that provides additional hydrogen source for the cathodic reactions. The annealed specimen with coarser grains was more corrosion resistant than the other specimens.

![Figure 5. Comparison of weight loss (WL) specimens with and without HAc for heat treated samples.](image)

**4. Conclusions**
The work studied the corrosion behaviour of heat treated steel specimens in CO₂/HAc containing media. Based on the results discussed in this work, the summary is as follows:

4.1. Heat treatment was found to affect the corrosion rates. The annealed specimen with coarser grain displayed better corrosion resistance. The corrosion rate results for annealed specimens were 35% lower than the other heat treated specimens.

4.2. The corrosion behavior of as-received specimens was similar to that of normalized steel specimens.

4.3. The presence of acetic acid was found to aggravate the overall corrosion rates by 30% to 55% in CO₂/HAc environment. At pH 5.5, there is 15% undissociated HAc in the solution that can readily provide additional hydrogen ion for cathodic reaction.

**Acknowledgement**
The authors would like to acknowledge the financial assistance received from Universiti Teknologi PETRONAS to carry out this work. Facilities provided by Centre for Corrosion Research are gratefully acknowledged.

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