Effect of Hydrogen Corrosion on Key Mechanical Properties of 45 Steel

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Abstract. To study the influence of hydrogen corrosion on mechanical properties of materials, this paper adapted 45 steel to determine each mechanical property parameter of 45 steel by tensile test method under different corrosion concentration and time as well as different states, including non-hydrogen escape and hydrogen escape. And the changing rule of strength index and plastic index of material during the process of hydrogen corrosion was obtained. The result shows that the strength index of material just has few changes, its yield strength fluctuates within -5.6Mpa and 7.8Mpa and tensile strength reduces by about 2%. After corroding, the plastic index reduces obviously and it is mainly affected by corrosion concentration whether it is in non-hydrogen escape state or in hydrogen escape state. Despite that the plastic index of hydrogen escape state is higher than that of non-hydrogen escape state, it still is less than the original value. In the inner of metal, the influence of diffused hydrogen on plastic index is stronger than that of solid solution hydrogen.

1. Introduction

Recent year, the amount of laying pipes of oil and natural gas increases sharply at home and abroad. Oil and natural gas not only involve the infrastructures of city development, energy supply and petrochemical engineering, but also become the basic condition for human life and economy development. Natural gas contains the aggressive medium, whose main injurious ingredient includes carbon dioxide, hydrogen sulfide, oxygen and water. The wet hydrogen sulfide environment is formed by the combined action of water and hepatic gas that will cause the variation of the strength and plasticity of metals under certain pressure, temperature and moisture conditions [1-2]. The Chinese and foreign scholars have made lots of researches concerning hydrogen embrittlement problem and obtained different results. Some scholars believe that the hydrogen degrades strength properties while others think that hydrogen increases strength properties or has no influence.

The main reason for the diffusion of hydrogen is that the metals exist concentration gradient [3]. In the inner of metal, hydrogen exists with the atomic state and its concentration distribution increases and then decreases from outside to internal concentration. When the corroded metal material is placed in the air, the hydrogen atom moves to the external metal, thus separating from metal. As for the diffusion rate of hydrogen, Chen et al. [4-5] found that the mobility of hydrogen at room temperature was strong and its coefficient of diffusion was relatively large so that it was necessary to consider the influence of diffused hydrogen on experimental results in the course of the experience. Taking 45 steel material widely applied in engineering as research objective, this paper studied the influencing rule of hydrogen corrosion process on mechanical properties of materials and difference between the
mechanical properties of materials after hydrogen escape and the original state or non-hydrogen escape state, which provides support for the research on the hydrogen corrosion.

2. Experiment

2.1. Sample
The paper studied the 45 steel material which was widely used in the engineering. The chemical composition and basic mechanical property of 45 steel are shown in Table 1 and Table 2. According to national GB T228.1-2010, this paper applied circular sample, whose gauge length L is 50mm and diameter D is 8mm (other sizes are shown in Figure 1). Before the experiment, the surface of the sample was dried after deoiling acetone and cleaning alcohol.

| Element | C       | Si      | Mn       | P       | S       | Cr   | Ni  | Cu  |
|---------|---------|---------|----------|---------|---------|------|-----|-----|
| Mass percentage/% | 0.42-0.50 | 0.17-0.37 | 0.50-0.80 | ≤0.035 | ≤0.035 | ≤0.25 | ≤0.25 | ≤0.25 |

Table 1. Chemical composition of 45 Steel.

Table 2. Mechanical properties of 45 steel.

| $R_e$ Mpa | $R_m$ Mpa | $A$ % | $Z$ % |
|-----------|-----------|-------|-------|
| 405.16    | 703.77    | 19.3  | 48.1  |

Figure 1. Dimension of sample.

2.2. Experiment environment
Based on the regulations of NACE TM0284, the corrosion environment in this paper was produced by standard class A solution (5% NaCl, 0.5% glacial acetic acid and 94.5% deionized water) with the input H$_2$S gas with different volume at room temperature. The selected corrosion of environmental concentrations in this paper were 200ppm, 400ppm, 800ppm and 1600ppm. The corrosion of environmental concentration was tested regularly via iodometric method.

2.3. Test grouping
This research was divided into two parts: the first part is the research concerning key mechanical properties of materials under the non-hydrogen escape state; the second part is to study key mechanical properties of materials under the hydrogen escape state. The non-hydrogen escape state refers to the situation that the sample is put into the etchant solution with normal concentration, immersed for a specified time and tested immediately after removal. Under this state, the hydrogen content in sample equals to the sum of solid solution hydrogen and diffused hydrogen. The divided groups of the tests under non-hydrogen escape state are shown in Table 3. And three tensile samples were selected for each corrosion time and concentration.

Hydrogen escape state means that after the sample reaches the specified corrosion time, the sample is taken out, dried and placed in room temperature for 24 hours for dehydrogenase treatment, and then relevant performance is tested. Under this state, part of the diffusion hydrogen escapes from the inner test piece and most of the hydrogen content in the specimen is solid solution hydrogen. The time and concentration of hydrogen escape is the same as that of non-hydrogen escape.
Table 3. Group design of corrosion experiments.

| Concentration gradient | 200ppm | 400ppm | 800ppm | 1600ppm |
|------------------------|--------|--------|--------|---------|
| Time                   |        |        |        |         |
| 24h                    | A1     | A2     | A3     | A4      |
| 48h                    | A5     | A6     | A7     | A8      |
| 72h                    | A9     | A10    | A11    | A12     |
| 96h                    | A13    | A14    | A15    | A16     |

3. Test result and analysis

By tensile test, the strength and plastic index of 45 steel under different test conditions were obtained, as shown in Table 4. Each data point in the following figure represents the average value of the results of three samples and the black horizontal line represents the original value.

Table 4. Performance Index of 45 Steel Materials in Hydrogen Corrosion Process.

| The state of non-hydrogen escape | The state of hydrogen escape |
|----------------------------------|-----------------------------|
| 200ppm                           | 400ppm | 800ppm | 1600ppm | 200ppm | 400ppm | 800ppm | 1600ppm |
| yield strength /Mpa              |        |        |        |        |        |        |        |
| 24h                               | 409.45 | 408.85 | 407.98 | 405.31 | 409.02 | 400.78 | 408.43 | 406.66 |
| 48h                               | 401.06 | 404.56 | 409.59 | 409.61 | 404.99 | 401.82 | 405.92 | 410.02 |
| 72h                               | 412.99 | 407.29 | 412.34 | 402.87 | 407.69 | 404.92 | 410.02 | 410.77 |
| 96h                               | 405.78 | 406.71 | 411.28 | 399.47 | 405.26 | 400.16 | 406.47 | 403.71 |
| Tensile strength /Mpa            |        |        |        |        |        |        |        |
| 24h                               | 691.15 | 695.57 | 695.63 | 692.83 | 687.85 | 686.10 | 688.10 | 691.01 |
| 48h                               | 678.79 | 685.03 | 689.98 | 700.01 | 684.82 | 687.74 | 686.66 | 688.76 |
| 72h                               | 680.51 | 687.10 | 692.76 | 693.55 | 685.13 | 692.13 | 696.99 | 696.47 |
| 96h                               | 681.39 | 691.28 | 694.57 | 698.09 | 686.06 | 691.90 | 693.72 | 694.33 |
| Elongation /%                     |        |        |        |        |        |        |        |
| 24h                               | 16.97  | 17.17  | 15.20  | 14.55  | 18.40  | 18.57  | 18.50  | 17.30  |
| 48h                               | 16.77  | 16.53  | 15.67  | 13.37  | 18.47  | 18.20  | 17.83  | 16.37  |
| 72h                               | 17.07  | 14.60  | 16.20  | 13.05  | 18.17  | 17.53  | 16.97  | 16.20  |
| 96h                               | 15.80  | 15.37  | 13.70  | 12.57  | 17.90  | 17.65  | 17.65  | 16.80  |
| Shrinkage of section /%           |        |        |        |        |        |        |        |
| 24h                               | 32.17  | 33.17  | 26.57  | 28.10  | 44.00  | 42.53  | 44.03  | 38.03  |
| 48h                               | 34.83  | 32.20  | 30.90  | 23.53  | 41.03  | 40.30  | 42.40  | 37.87  |
| 72h                               | 34.60  | 26.80  | 35.27  | 23.75  | 41.93  | 41.27  | 38.73  | 36.65  |
| 96h                               | 32.80  | 30.73  | 27.80  | 24.53  | 42.13  | 40.75  | 40.90  | 38.20  |

3.1. Influence of hydrogen-type corrosion on yield strength

(a) The state of non-hydrogen escape.  
(b) The state of hydrogen escape.

Figure 2. The variation of yield strength with corrosion time.

(a) The state of non-hydrogen escape.  
(b) The state of hydrogen escape.

Figure 3. The variation of yield strength with corrosion concentration.

From figure 2 and figure 3, it is found that under different states, the yield strength fluctuates as hydrogen corrosion time and concentration increase, whose difference with the original value does not exceed the range [-5.6Mpa, 7.8Mpa].
3.2. Effect of hydrogen corrosion on tensile strength

From Figure 4 and Figure 5, it is known that the tensile strength of 45 steel after corrosion is lower than that of original state and the average values of tensile strength of all samples under non-hydrogen escape state and hydrogen escape state are 690.51MPa and 688.74MPa respectively. The Figure 4 shows that, the trend of tensile strength of non-hydrogen escape state with the increasing of corrosion time is almost the same as that of hydrogen escape state, both of which are the para-curve with an opening facing up. Its lowest values (678.79MPa and 684.82Mpa respectively) occur in 200ppm environment for 48 hours. Figure 5 demonstrates that the changing rules of tensile strength value of non-hydrogen escape and hydrogen escape state are basically the same. When the corrosion concentration is 200ppm, the decrease is the largest and then the tensile strength increases with the increasing of corrosion concentration. However, in conclusion, the difference between tensile strength after hydrogen corrosion and original strength is 2%.

3.3. Influence of hydrogen corrosion on elongation

As for the influence of corrosion time, from Figure 6(a), it is found that after the corrosion of hydrogen, the whole elongation decreases with the increasing of corrosion time. At the same time, under the environment that corrosion concentration equals to 1600ppm, the decline of elongation is the most obvious. The distance among four curves are relative large, which shows that the obtained data are discrete. From Figure 6(b), it is known that after placing in air for 24 hours, the elongation tends to decline as the corrosion time increases. However, compared with Figure 6(a), the obtained elongation value under hydrogen escape state approximates the original performance of material and the distance among the curves is relative closer, which proves that its dispersity of data is better than that of non-hydrogen escape state.

Figure 7(a) and Figure 7(b) show that with the same corrosion time, the elongation of material decreases as the corrosion concentration increases. Under the same non-hydrogen escape state, from the slope of curves in Figure 6(a) and Figure 7(a), it is found that the elongation values decreases sharply along the direction of corrosion concentration, which demonstrates that the influence of concentration on elongation is obvious.
By comparing the differences among the elongation under non-hydrogen escape state, hydrogen escape state and original state, the average values of 48 data of non-hydrogen escape and 48 data of hydrogen escape state were obtained without considering the influence of corrosion time and concentration gradient on the test, as shown in Figure 8. The average value of non-hydrogen escape state decreases by 20.94% than that of original state. The extension rate of hydrogen escape state recovers, which is 9.05% lower than the original value.

![Figure 8. Comparison of elongation in different states.](image)

![Figure 9. The variation law of elongation with corrosion concentration.](image)

To study the effect of corrosion concentration on elongation, the averages values of 12 experimental data of 4 kinds of corrosion time under different corrosion concentrations were obtained, as shown in Figure 9. From the figure, the elongation under two states has linear relationship with corrosion concentration. The linear fitting results are shown in formula 1 and 2.

\[
A_{\text{non-hydrogen escape}} = 16.9780 - 0.0023C_{H_2S} \tag{1}
\]

\[
A_{\text{hydrogen escape}} = 18.5616 - 0.0013C_{H_2S} \tag{2}
\]

where \(C_{H_2S}\) represents the concentration of hepatic gas.

Based on the fitting curves of non-hydrogen escape and hydrogen escape tests, it is found that the elongation of hydrogen escape state with all corrosion concentrations is larger than that of non-hydrogen escape state. This shows that after placing for 24 hours, the hydrogen content in the material decreases and part of plastic property of material recovers. Nevertheless, compared with the original states, the elongation still declines by around 10% after placing for 24 hours and it does not recover to the original state. This is because the hydrogen in the metal exists in the state of solid solution, which requires high temperature and pressure process to reach the dehydrogenase state. However, the test method in the paper is to place the specimen at room temperature and pressure so that the state of being completely dehydrated could not reach. Despite that, the test result also shows that hydrogen has two existence states in metal, including diffusible hydrogen and solid solution hydrogen. Both of these states would have an obvious impact on plastic property of material.

In addition, from the gradient of two curves, it is known that the gradient of non-hydrogen escape state is -0.0023, while the gradient of hydrogen escape state is -0.0013. That proves that the difference of elongation between non-hydrogen escape experiment and hydrogen escape experiment also gradually increases with the increasing of corrosion concentration and the content of diffusible hydrogen entering into the inside metal also continuously increases.

3.4. Influence of hydrogen corrosion on reduction of area

Figure 10 shows the effect of corrosion time on reduction of area. Figure 10(a) and Figure 10(b) demonstrate that with the same corrosion concentration, the variation of reduction of area of the sample basically shows a horizontal trend whether it is in non-hydrogen escape state or hydrogen escape state. The corrosion time just has limited effect on the reduction of area.
Figure 11 shows the changing rule of reduction of area with the variation of corrosion concentration. From Figure 11(a), it is known that under the state of non-hydrogen escape, the reduction of area decreases sharply as the corrosion concentration increases. Figure 11(b) shows that the changing trend of reduction of area of hydrogen escape state is similar with that of non-hydrogen escape state, but its curve gradient and difference with original performance is less than that of non-hydrogen escape state. From the analysis above, it is found that the influence of corrosion concentration on the reduction of area is stronger than that of corrosion time.

Figure 10. The variation of Shrinkage of section with corrosion time.

The average values of 48 data of non-hydrogen escape state and 48 data of hydrogen escape state were obtained, as shown in Figure 12. From figure, it is obviously seen that the contraction percentages of section of original state, non-hydrogen escape state and hydrogen escape state present the total different values. The after corrosion is lower than the original value. Compared with the original value, the contraction percentages of section of non-hydrogen escape state and hydrogen escape state decrease by 37.87% and 15.27% respectively. And that of hydrogen escape state is 26.67% higher than non-hydrogen escape state.

Figure 12. Comparison of Shrinkage of section in different states.

Figure 13. The variation of Shrinkage of section with corrosion concentration.

Figure 13 shows the changing rule of contraction percentages of section of non-hydrogen escape state and hydrogen escape state along with the variation of corrosion concentration. After linear fitting, formula 3 and 4 were obtained.

\[
Z_{\text{non-hydrogen escape}} = 34.0060 - 0.056 C_{H_2S} \\
Z_{\text{hydrogen escape}} = 40.2504 - 1.032 \times 10^{-4} C_{H_2S}
\]  

(3)  

(4)

Similar with the rule of elongation, the changing rule of reduction of area also demonstrates the influence of diffused hydrogen and solid solution hydrogen on the plastic properties of materials. Under the non-hydrogen escape state, hydrogen content in specimen equals to the sum of diffused hydrogen and solid solution hydrogen. For hydrogen escape state, part of diffused hydrogen escapes and the rest content in specimen is solid solution hydrogen. The declining of hydrogen content makes reduction of area increase. However, from Figure 13, it is found that the declining trend of reduction
of area of non-hydrogen escape state specimen is higher than that of hydrogen escape state. That suggests that diffusible hydrogen has a more obvious impact on reduction of area.

4. Conclusions
This paper studies the changing rules of key strength index and plastic index of 45 steel with different corrosion time and concentration as well as different states, including non-hydrogen escape state and hydrogen escape state. The conclusions as follows:

(1) After corrosion of hydrogen, yield strength value of 45 steel under two state fluctuates, compared with the original value. But their difference is only within 1.38%. The tensile strength is lower than the original value and the difference between tensile strength and original value is 2%. There is no obvious difference of strength index of material between two states and original state.

(2) The plastic index (elongation and reduction of area) of material after corrosion is obviously less than the original value and the influence of hydrogen on the performance of the material mainly focuses on the plastic index. Despite being less influenced by corrosion time, two plastic indexes drop rapidly and linearly. Compared with non-hydrogen escape state, the plastic index of hydrogen escape sample rises again after placing at the room temperature environment for 24 hours, but it is still less than the original value. After corrosion of sample, diffusible hydrogen in metal has a larger influence on plasticity than solid solution hydrogen.

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