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Experimental Study on Mechanical Properties Degradation of TP110TS Tube Steel in High H_2S Corrosive Environment

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Abstract: The research on casing corrosion in sour environment by a synergism of sweet corrosion and H_2S corrosion has become the basis of casing selection and casing string safety evaluation with more and more sour reservoirs containing high H_2S concentration being developed. It is essential to scientifically utilize casing service ability and reasonably control production rate of gas well to achieve the effective and safe developing of gas resources during the safety period of casing service with a precise casing life prediction. Scanning electron microscopy and tensile testing were applied to investigate the corrosion of TP110TS tube steel in stimulant solution with carbon dioxide (CO_2) and hydrogen sulfide (H_2S) at variable conditions of P_{CO2}/P_{H2S}, temperature and time. This paper especially focused on the degradation of mechanical properties (elastic modulus, yield strength and tensile strength) of test specimens subjected to corrosion. Experimental results suggest that the fracture mode will transit from ductile fracture before corrosion to brittle fracture after corrosion and the mechanical properties will experience obvious degradation when the specimens were exposed to corrosive environment. Service life prediction model of casing was established on the basis of experimental observations and results.

Keywords: CO_2/H_2S corrosion; TP110TS tube steel; mechanical properties degradation; service life prediction

1 Introduction

It is very necessary to investigate the corrosion mechanism and regularity of CO_2 corrosion and H_2S corrosion with more and more sour reserviors containing high H_2S and CO_2 being developed. Research about synergistic effect of CO_2 and H_2S

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is limited although the research when CO_2 or H_2S exists separately has already made considerable progress. Some scholars such as G.Fierro [Fierro et al (1989)], K.Masamura [Masamuraet al(1987)], Ma Houyi[Ma et al(2000)] illustrated the mechanism of sour environment corrosion by using experimental study. Z.F.Yin [Yin.Z.F et al (2008)] dealt with corrosion behavior of SM 80SS tube steel in stimulant solution containing H_2S and CO_2. Ren.C.Q et al [Ren.C.Q et al (2005)] focused on the relationship between corrosion rate (CR) and the partial pressure of H_2S and CO_2 in system and established the fitting equation between CRs and P_{CO2}/P_{H2S}.The effect of corrosion on casing has become increasingly important in the evaluation of casing string safety which experiences severe corrosion by the sour gas reservior characterized by high H_2S concentration, high pressure and high production rate. Hydrogen sulfide stress cracking will occur when H_2S and tensile stress coexist simultaneously which can result in casing life a sharp drop [M.A Stair et al(1986) and Crusco (1981)]. Casing service ability can be scientifically utilized during the safe service period to achieve the effective and safe developing of gas resources on the base of a precise prediction of casing life. Comprehensive study regarding the mechanical properties degradation of casing after corrosion in sour environment was carried out based on experiments which were conducted by simulating the actual service conditions. The life prediction model was established using the results and observations founded in experiments.

2 Experiment

2.1 Experimental material and apparatus

Two types of test specimens for different purposes were made from TP110TS tube steel whose chemical composition was shown in Table 1.Rectangular test specimens, sized 50mm×10mm×3mm with hole diameter 6mm,were specifically used to test corrosion rate in the absence of environmental stress. Fig.1 shows the size and shape of tensile test specimens which are designed and manufactured according to GB 6397-86 standard to meet the requirements of mechanical property test after corrosion.

Table 1: Composition of TP110TS tube steel (wt%)

C	Si	Mn	P	S	Cr	Mo	Ni	Fe
0.25	0.2	1.4	0.009	0.003	0.15	0.01	0.012	BAL

Tensile test specimen can also be used to measure corrosion rate in the presence of environment stress. Before the test, the surface of this two types of specimen were polished with grit silicon carbide papers progressively from 400 to 1000 grades

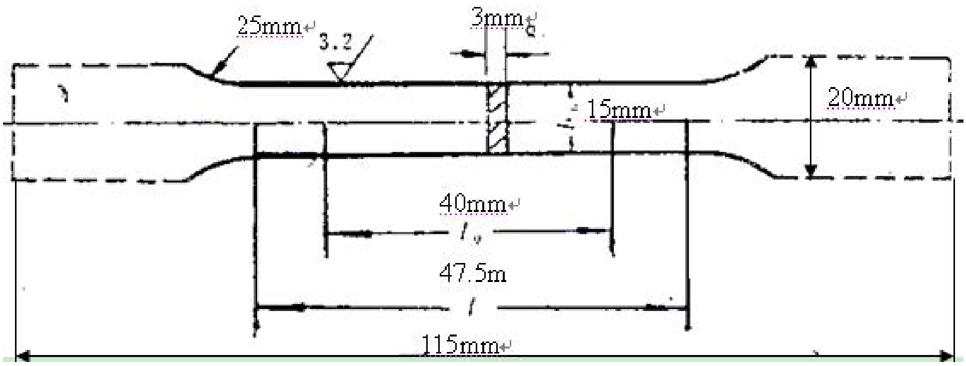


Figure 1: Size of tensile test specimen

to eliminate the effect of machine processing. The corrosion behavior of specimen was evaluated by using an autoclave (34.4MPa) made by Cortest Company for high temperature and high pressure condition. Fig. 2 shows the schematic illustration of the autoclave.

Instron 1341 tensile testing machine was utilized to test the mechanical properties of corroded specimens and fracture surface morphologies of corroded specimen were observed by Cambridge S360 scanning electron microscopy (SEM).Four-point loading approach was taken to apply given load to the specimen which was in consistent with NACE TM0177-2005 standard[NACE(2005)]. Fig.3 shows the stress loaded tool and its stress loading mechanism.

2.2 Experimental conditions

Concentrations of various ions of the stimulant solution which was simulated with the actual service environment were listed in Table 2. The system was given required CO_2 and H_2S partial pressure, but the total pressure of the test was kept at 20MPa by pumping pure nitrogen to the system. The partial pressure of H_2S, temperature and corrosion time was altered respectively to investigate the effect of those factors on corrosion characteristics in the absence of environment stress. In the case of stress loading, tensile test specimens were loaded with 30%σs, 70%σs and 90%σs stress respectively while keeping other conditions unchanged to find the law of stress influence on casing corrosion.

2.3 Experimental procedures

(1) In the case of no stress loading, each group contained four rectangular specimens and 3 tensile test specimens. All specimens were degreased with trichloroethane

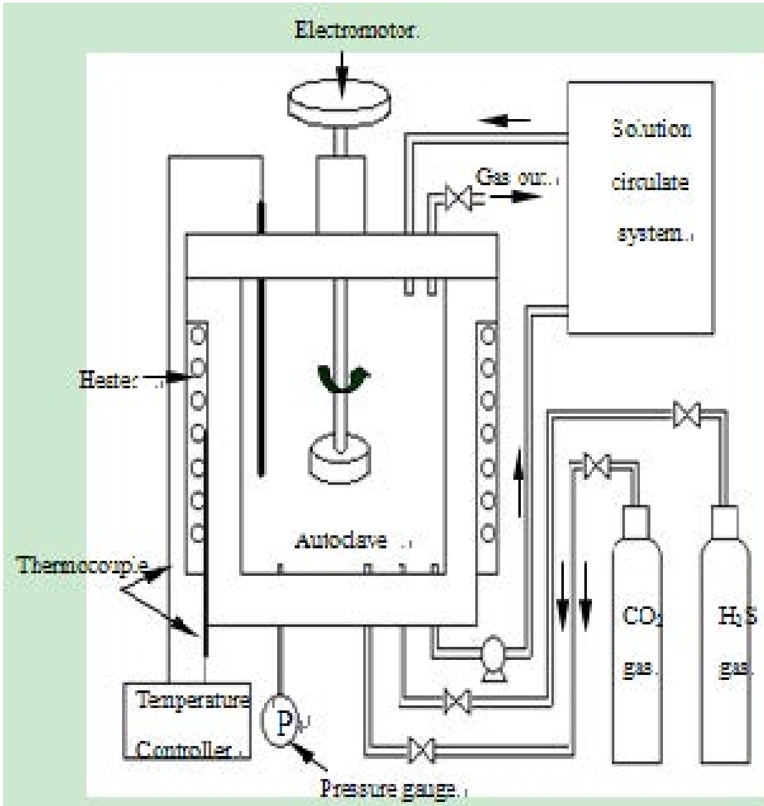


Figure 2: Schematic illustration of corrosion autoclave

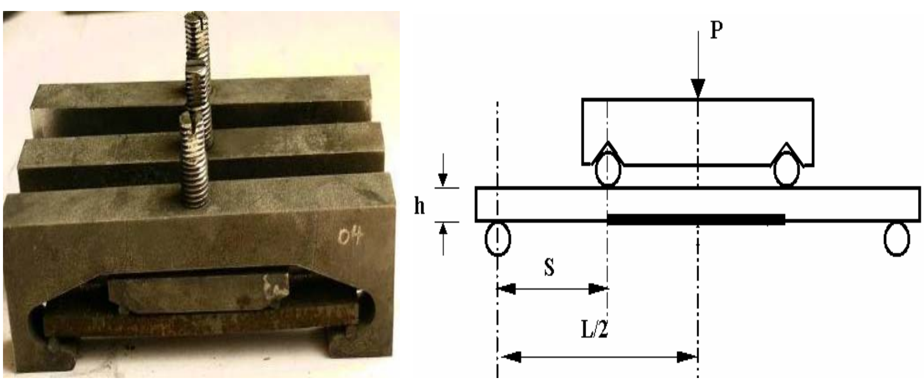


Figure 3: Schematic diagram of stress loading tool

Table 2: Concentration of various ions of stimulant solution

Cl^-(mg/L)	Ca^{2+}(mg/L)	Mg^{2+}(mg/L)	Na^+(mg/L)	K^+(mg/L)	PH
50000	15000	6000	1500	1000	4.5

and rinsed with acetone, weighted with a precision of 0.1 mg after drying. Rectangular specimens were fixed on the special fixture and tensile test specimens placed around the fixture uniformly. In the presence of environment stress, six stress loading tools with six tensile specimens were put into the autoclave each time. Three tensile test specimens were measured for corrosion rate and others for testing mechanical properties.

(2) Seal testing the autoclave to 20MPa with nitrogen, then the solution was deoxygenated by pure nitrogen for 6 hours. After desired temperature was reached, the system was given required partial pressure and nitrogen was pumped up to total pressure (20MPa).

(3) After the corrosion test, all corroded specimens were removed from the autoclave and rinsed with deionized water. Then the corroded specimens were divided into two groups: the corroded specimens for measuring corrosion rate were descaled with special solution (the solution:500mlHCl (ρ=1.19g/L), 20g hexamethylenetetramine and 500ml distilled water) rinsed with absolute alcohol, dried in nature state and weighted again with a precise of 0. 1 mg and then the corrosion rate can be calculated. Other corroded specimens were rinsed with distilled water and not descaled for testing mechanical properties at earliest time. The corroded specimens were tested by Instron 1341 tensile testing machine with 1mm/min stretching rate until the specimen fractured. Cambridge S360 scanning electron microscopy (SEM) was utilized to observe fracture surface morphology to estimate the SCC sensitivity of corroded specimens.

3 Experimental results

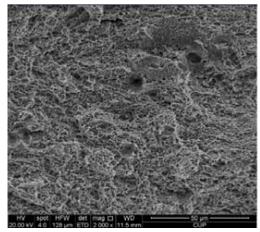
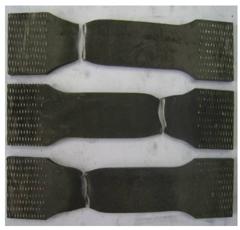
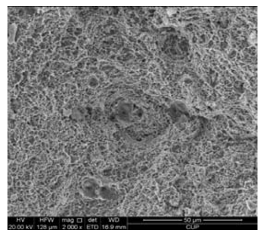
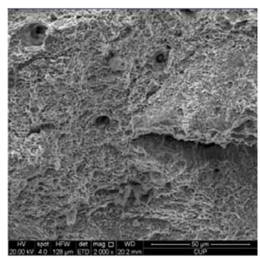
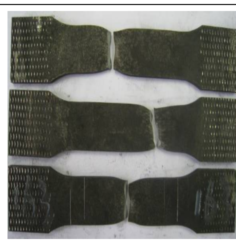
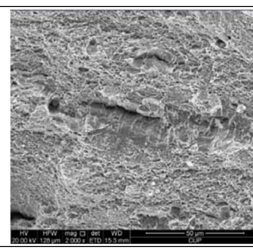
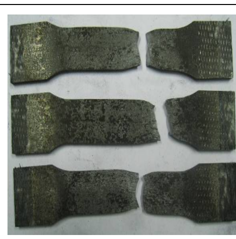
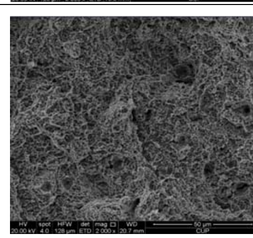
3.1 Corrosion rate and fracture surface morphology

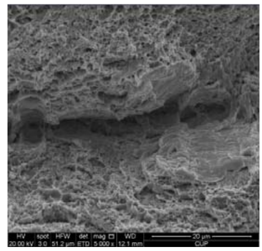
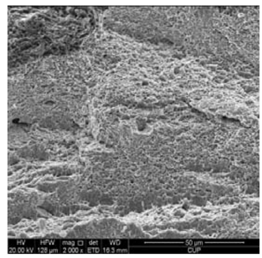
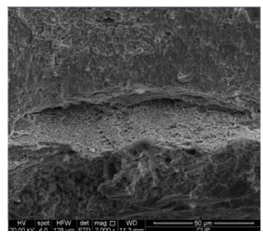
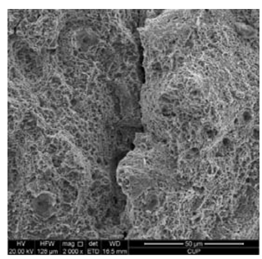
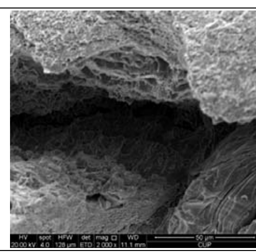
According to weight loss test and the size of specimens, corrosion rate can be calculated by formula as follows:

$$V_{corr} = \frac{\Delta W}{\rho \cdot S \cdot T}$$

Where ΔW is weight loss (g), ρ is material density (g/cm^3), S is the surface area of specimen (mm^2), T is corrosion time (year). Table 3 shows experimental conditions, corrosion rate, weight loss ratios and fracture surface morphology.

Table 3: Corrosion rate and fracture surface morphology of corroded sample

	experimental conditions	corrosion rate(mm/a)	weight loss ratio	fractured specimen	high magnification morphology
blank					
1	H_2S: 0.7MPa, CO_2: 1.2MPa, Temp.100℃, Time:360hrs, Total Pressure, (**T.P**):20MPa	0.1286	0.0054		
2	H_2S:0.7MPa, CO_2:1.2MPa, Temp.100℃, Time:168hrs, T.P:20MPa	0.1515	0.0026		
3	H_2S:2.0MPa, CO_2:1.2MPa, Temp.100℃, Time:360hrs, T.P:20MPa	0.1660	0.0063		
4	H_2S:2.0MPa, CO_2:1.2MPa, Temp.50℃, Time:168hrs, T.P: 20MPa	0.2635	0.0053		

5	H_2S: 2.0MPa, CO_2:1.2MPa, Temp.100℃, Time:168hrs, T.P:20MPa	0.3005	0.0052		
6	H_2S: 2.0MPa, CO_2:1.2MPa, Temp.100℃, Time:168hrs T.P:20Mpa, stress:30%σs	0.3036	0.0044		
7	H_2S: 2.0MPa, CO_2:1.2MPa, Temp.100℃, Time:168hrs, T.P:20Mpa, Stress:70%σs	0.3333	0.0054		
8	H_2S: 2.0MPa, CO_2:1.2MPa, Temp.100℃, Time:168hrs, T.P:20Mpa, Stress:90%σs	0.3724	0.0048		
9	H_2S: 0MPa, CO_2:1.2MPa, Temp.100℃, Time:168hrs, T.P:20MPa	1.0899	0.0019		

3.2 Yield strength and weight loss ratio

The average value of yield strength, tensile strength and elastic modulus at various weight loss ratios after removal the outlier was shown in Table 4. Weight loss ratio is defined as weigh loss of specimen after corrosion divided by the original weight of specimen before corrosion.

Table 4: Measured mechanical properties and weigh loss ratio

group	weight loss ratio	yield strength (MPa)	tensile strength (MPa)	elastic modulus (GPa)
blank		758.0	827.5	209.7
1	0.0026	732.2	806.9	211.2
2	0.0044	710.3	780.8	200.3
3	0.0048	704.9	773.8	185.3
4	0.0052	703.1	775.3	211.4
5	0.0053	697.1	759.7	197
6	0.0054	693.3	770.5	190.2
7	0.013	672.8	749.2	190
8	0.019	658.1	721.6	185.2

4 Conclusions

(1) Experimental results indicate that yield strength and elastic modulus of tube steel degradate seriously due to wall thickness thinning and hydrogen-induced softening in H_2S corrosive environment. The degradation of mechanical properties should be considered in predicting the service life of tubes.

(2) Fracture mode will transit from ductile fracture before corrosion to brittle fracture after corrosion. The degree of brittle fracture will increase with the increasing of corrosion rate and will be more intense with the higher corrosion rate, which indicates that the tested material is sensitive to SCC.

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