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Effect of Temperature on the Corrosion Behaviours of L360QCS in the Environments Containing Elemental Sulphur and H_2S/CO_2

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The effect of temperature on the corrosion behaviours of L360QCS in H_2S, CO_2 and elemental sulphur environments are investigated. The corrosion weight-loss rate, microscopy, chemical compositions and phase compositions of corrosion products are studied by means of the weight-loss analysis, SEM and XRD techniques. As shown, the corrosion rate increased greatly with an increase of the temperature, and the corrosion scale is dropped off easily because of the weak adhesion force between the matrix and the corrosion products. The composition and structure analysed by energy-dispersive x-ray spectroscopy (EDS) and XRD show that the corrosion product scales are composed of cubic FeS and little tetragonal FeS.

Досліджено вплив температури на режими корозії L360QCS в атмосфері H_2S, CO_2 та атомарної сірки. Швидкість корозії, яка вимірюється за втратами ваги, мікроскопія, хемічний та фазовий склад продуктів корозії визначалися аналізою втрати ваги, СЕМ та рентґеноструктурною аналізою (РСА). Показано, що швидкість корозії сильно збільшується з температурою, і корозійна жужелиця легко відпадає через слабку силу адгезії між матрицею та продуктами корозії. Дослідження складу та структури методами рентґеноспектральної електронно-зондової мікроаналізи та РСА показали, що жужелиці продуктів реакції складаються з кубічного FeS та незначної частки тетрагонального FeS.

Исследовано влияние температуры на режимы коррозии L360QCS в атмосферах H_2S, CO_2 и атомарной серы. Скорость коррозии, измеряемая по потере веса, микроскопия, химический и фазовый состав продуктов коррозии определялись анализом потери веса, СЭМ и рентгеноструктурным анализом (РСА). Показано, что скорость коррозии сильно возрастает с температурой, и коррозионная окалина легко отпадает благодаря слабой силе адгезии между матрицей и продуктами коррозии. Исследования состава и структуры методами рентгеноспектрального электронно-зондового микроанализа и РСА показали, что окалины продуктов реакции состоят из кубического FeS и небольшой части тетрагонального FeS.

Key words: elemental sulphur, corrosion, L360QCS, microstructure.

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1. INTRODUCTION

More and more sour oil and gas fields containing higher partial pressure H_2S and CO_2 are being exploited for sweet fields being depleted and higher oil price. The pipeline used in the environments containing high pressure H_2S are often corroded, especially in the case of elemental sulphur existence in the environment. The sulphur will be dissolved out in high H_2S partial pressure environment as the solubility of sulphur in solution decreases with the decrease of pressure and temperature from bottom to top of oil or gas reservoir [1]. The corrosion problem is the key point to the development of acid gas or oil fields in the environment containing high H_2S/CO_2 pressure, elemental sulphur, and salinity brine.

A concern in the production and transportation sour oil and gas is the corrosion caused by the acid gases CO_2 and H_2S. Many measurements have been taken to mitigate H_2S and CO_2 corrosion, such as using corrosion inhibitor, stainless steel and resistant HIC pipeline [2–5]. At present, carbon steel is in general more cost-effective for oil and gas facilities and hence is the most widely used material option [1]. However, a few reports involve in the role of the temperature in the corrosion of L360QCS in the environment of H_2S/CO_2 and salinity brine as well as elemental sulphur existence.

L360QCS is one of the low alloy carbon steels, which are widely used in the gathering system in oil or gas field containing H_2S and CO_2 gases. Its service temperature is almost lower than 90°C, which is below the sulphur melting point (112.8°C). Therefore, in a given paper, the effect of temperature on the L360QCS corrosion was studied below 90°C.

2. EXPERIMENTAL

The test samples were cut from L360QCS pipeline steel. Their chemical compositions (wt.%) are as follow: C—0.13, Si—0.4, Mn—1.5, P—0.02, S—0.003, Cr—0.03, Mo—0.1, Ni—0.3, Ti—0.04, Fe—balance. The metallographic structure of L360QCS is tempered sorbitol.

The test solution was prepared by simulating some oil gas field in China. The total mineralization of the solution is 67900 mg/l, and the mass concentration of cations is $2.61 \cdot 10^4$ mg/l, while the anionic mass concentration is $4.18 \cdot 10^4$ mg/l. The water type is $CaCl_2$ with the pH 7.97. The H_2S and CO_2 partial pressures are 1.5 MPa and 1.0 MPa, respectively. The elemental sulphur was used at the ratio of 10 g per litre solution to simulate the deposited environment. The corrosion behaviours of L360QCS at different temperatures were studied. The simulation experiments were conducted during 72 hours at 30°C, 50°C and 90°C.

Three standard corrosion coupons are cut from L360QCS pipeline. Each coupon was polished to 800 grits abrasive paper. The samples were carefully weighted after acetone washing. The corrosion progress with no oxygen participation is run at the high temperature and high-pressure reaction autoclave, in which a special holder fixes the samples.

After the experiment, the samples were taken out from the reaction autoclave and cleaned with ethyl alcohol before drying. The corrosion weight loss method is used to research the effect of temperature on the corrosion behaviours of L360QCS in the environments containing elemental sulphur and H_2S/CO_2, and SEM, EDS and XRD are used to analyse the corrosion production scales.

3. RESULT AND DISCUSSION

3.1. Effect of Temperature on the Corrosion Rate

Figure 1 shows the corrosion rate of L360QCS at different temperatures. It was shown that the corrosion rate of L360QCS increased quickly with the increase of test temperature. The rate is 14 mm/a at 30°C, it reaches 50.5 mm/a at 50°C, and the rate rushes to 120.9 mm/a at 90°C. Therefore, in the wet H_2S/CO_2 environment with 10 g/l ele-

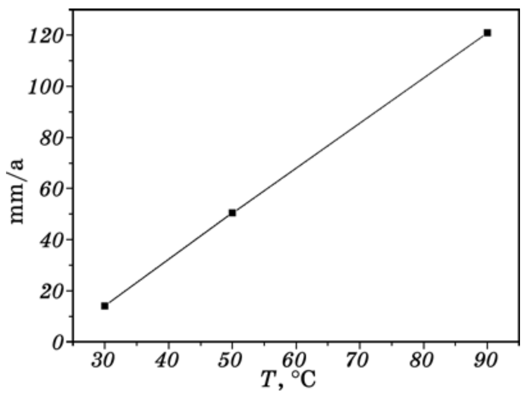

Fig. 1. The corrosion rates of L360QCS at different temperatures.

mental sulphur, the increase of temperature speeded up the corrosion rate rapidly even at the temperature lower than sulphur melting point.

The accelerated corrosion rate was also certificated by means of electrochemical method with the temperature increasing from 30°C to 80°C in sulphide corrosion environment [6]. The temperature raises the slope coefficient of Tafel anticathode curve. Meanwhile, the cathode reaction changed and the corrosion potential became more positive. Therefore, the temperature improves both anode and cathode reactions.

3.2. Effect of Temperature on Macromorphology

From the results above, we found that the temperature greatly affected the corrosion behaviours of carbon steel in the environment. Figure 2 shows the macromorphology of corrosion production of L360QCS at different temperatures and Fig. 3 shows the macromorphology of the matrix of homologous samples. It was shown that there was an obvious change in the corrosion shape with the increase of the temperature, the sample shape can keep the pervious shape after the corrosion at 30°C. However, it was far different from the basics shape after corrosion at 90°C.

It was also found that the morphologies of corrosion products are different at different temperatures. At the temperature of 30°C, the scale of corrosion production is very thin but compact, and it is not easy to exfoliate. There is lots of pitting on the surface of matrix, especially on the region around the edge of the sample. When it comes to 50°C, the scale becomes thicker, but much of the corrosion products exfoliate from the matrix, the inner layer is much more looser and thinner than those of at 30°C. The corrosion took on a uniform corrosion characteristics. When the temperature is raised to 90°C, the corrosion reaction is much more acute, most of the corrosion products dropped off from the sample. From the picture (*c*) in Fig. 2, we can see that there is only about a half of the sample left for the heavy corro-

Fig. 2. The macromorphology of corrosion products of L360QCS formed at different temperatures: 30°C (*a*), 50°C (*b*), 90°C (*c*).

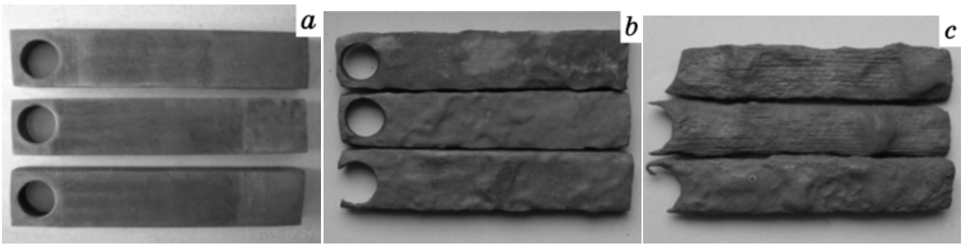

Fig. 3. The macromorphology of matrix after removing the corrosion products L360QS formed at different temperatures: 30°C (*a*), 50°C (*b*), 90°C (*c*).

sion.

3.3. Effect of Temperature on Micromorphology and Composition

In order to study the effect of temperature on micromorphology and composition of corrosion products of L360QCS, SEM and EDS were used to investigate the corrosion products. The micromorphology of the corrosion products on the surface of L360QCS formed at different temperatures is shown in Fig. 4.

At 30°C, the corrosion production scales are very flat and adhere to the matrix tightly. However, there are many irregular potholes in the film. When it comes to 50°C, the corrosion product scale becomes thicker, but the bond of the film is so weak that the part of corrosion scale is dropped off. From Fig. 4, it was found that the corrosion scales were composed of two layers. The outer layer can be easily torn off and the inner one is too thin and loose to protect the matrix of the sample, but the compositions are nearly the same. The outer layer is much more compact and consisting of regular FeS crystals. When the temperature reaches 90°C, the adhesive force between the corrosion production and matrix turns weaker, so, almost all of the products are dropped off.

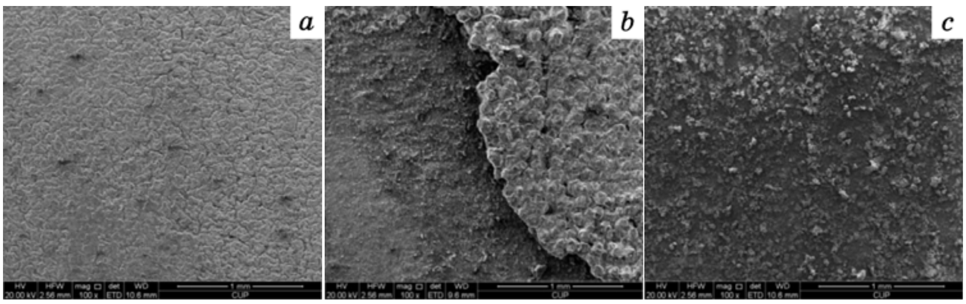

Fig. 4. The micromorphologies of corrosion products L360QS formed at different temperatures: 30°C (*a*), 50°C (*b*), 90°C (*c*).

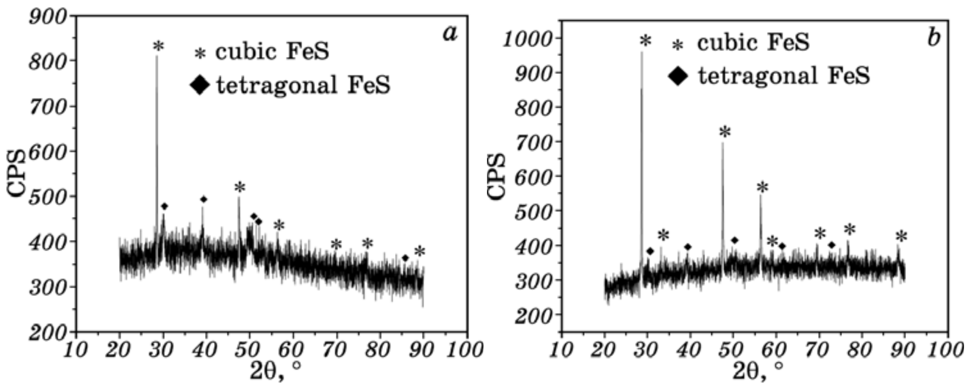

Fig. 5. XRD pattern of L360QCS after corrosion at different temperatures: 30°C (*a*), 50°C (*b*).

3.4. Effect of Temperature on the Structure of the Corrosion Production

The phase compositions of the corrosion production were analysed by x-ray diffraction. The results of the x-ray diffraction are shown in Fig. 5. The corrosion production of L360QCS pipeline are similar at different temperatures, which are composed of cubic crystal structure FeS and little square crystal structure FeS.

The corrosion of carbon steel in the environment of H_2O/CO_2 without sulphur has been researched by G. Firro [7] and K. Masamura [8]. If $P_{CO_2}/P_{H_2S} < 200$, the corrosion is mainly H_2S attacked. FeS film will be the first produced when the carbon steel is dipped into the corrosion solution, which will prevent the formation of $FeCO_3$ film. In our test, $P_{CO_2}/P_{H_2S} = 1.0/1.5 = 0.67$. Therefore, the corrosion reaction is mainly H_2S attacking especially in the environment containing sulphur deposition. The results of our test confirmed the point and there is no $FeCO_3$ in the production.

4. CONCLUSIONS

1. When the temperature is lower than sulphur melting point, the corrosion rate of L360QCS increases linearly dependent on the temperature.
2. At a higher temperature, the corrosion scale turn thicker and the adhesive force between the corrosion scale and metal matrix turns weaker.
3. At low temperature, the corrosion type is mainly local corrosion, when it comes to 50°C, the corrosion type becomes an uniform attack; at higher temperature of 90°C there are many corrosion grooves on the

sample surface.
4. The results of XRD show that the corrosion products are composed of cubic FeS crystal and less tetragonal FeS crystal. Temperature has little effect on the chemical composition of the corrosion production.

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