Effects of temperature on oxidation behaviours of 35CrMo in high temperature flue gas environment

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Abstract. The pipelines made by alloy 35CrMo are widely used in the process of flue gas injection. Therefore, corrosion behaviours of alloy 35CrMo have been investigated at varied temperatures, namely 120 °C, 150 °C, 200 °C and 250 °C, with same experimental pressure of 9 MPa and flus gas environment. Scanning electron microscopy was employed to examine the morphologies and microstructures of the oxide films. The results indicated that moderate temperature stands an essential role in the reaction mechanism and aggressive effects. In addition to increase in the diffusion rate of both alloy ions and corrosive gas, temperature can also reform the morphology of oxides by resulting in larger oxide particles and thicker oxide films, plus the transmission from needle-like oxides to spherical oxides.

1 Introduction

Flue gas injection is a tertiary recovery method in which the flue gas produced by boiler in heavy oil thermal recovery is processed and pressurized and then injected into the reservoir, mixing with residual crude oil to displace the crude oil. Besides approximately 79 ~ 85% N_2 [1], this gas mixture, which could lead to serious corrosion on carbon steels and alloys used in casings and pipelines, still contains 10 ~ 15% CO_2 and a little aggressive gas. Pan et al. [2] have conducted in-plant corrosion tests of five steel in a heating boiler to investigate the desulfurized flue gas corrosion coupled with deposits after flue gas desulfurization (FGD) unit and concluded that surface temperature of the steel was proved to be the key factor in the corrosion process.

The reaction mechanism and aggressive effects of flue gas on metals and alloys vary with different flue gas temperature ranges. At low flue gas temperature [3], when water vapour interacts with acid materials at the low temperature surface of metal wall, condensation would be achieved, leading to corrosion and decrease in apparatus life. At high flue gas temperature [4], sulphur, chlorine and alum salt corrosion are the main types of corrosion emerging at the surface on the side of gas, in which sulphur element corrosion is most common and relatively more serious. However, there are less literatures with regard

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to the effects of flue gas on carbon steels and alloys at specific temperature between high and low flue gas temperature at present. Consequently, to propose some reliable suggestions for choosing proper materials of casings and pipelines in oil filed, it is necessary and valuable to investigate the reaction mechanism and aggressive effects of flue gas on metals and alloys at moderate temperature.

The pipelines made by alloy 35CrMo are widely used in the process of flue gas injection. Therefore, with the flue gas generated by a boiler in Liaohe oil field in Liaoning Province of China acting as aggressive medium, corrosion behaviours of alloy 35CrMo have been investigated at different temperatures in this paper. Scanning electron microscopy (SEM) [5] was employed to examine the morphologies and microstructures of the oxide films. The results suggest an essential role played by moderate temperature in the reaction mechanism and aggressive effects. Besides increase in the diffusion rate of both alloy ions and corrosive gas, temperature can also change the appearances of oxides by leading to bigger oxide particles, thicker oxide films and the transmission from needle-like oxides to spherical oxides.

2 Experimental and instrumentations

Table 1 and Table 2 are the composition of the flue gas and alloy 35CrMo respectively. Alloy 35CrMo was cut into cubic pieces with dimensions of 8 mm x 6 mm x 5 mm. SiC sandpapers were used to smooth the cut materials, which were then soaked in ultrasonic wave cleaner with acetone for 30 min to degrease. Finally, cleaned by deionized water, these samples were put into the vacuum drying box to avoid air corrosion. Moreover, high–temperature tubular furnace (OTF-1200X-S, Kejing Co., Ltd) was the main equipment to proceed experiments and SEM was the crucial analysis tool.

In order to investigate the effect of temperature on corrosion behaviours of alloy 35CrMo, four discrete temperature points, namely 120 ℃, 150 ℃, 200 ℃ and 250 ℃, and four different time points namely 24 h, 48 h, 72 h and 96 h were set, with the same experimental pressure of 9 MPa and flue gas environment. Detailed experiments are listed in Table 3.

Table 1. Compositions of flue gas

Species	**O_2**	**CO_2**	**NO_2**	**H_2**	**H_2S**	**N_2**
Vol.%	7.000	11.000	0.005	0.001	0.001	Balance

Table 2. Composition of metal species in 35CrMo

Species		**C**	**Si**	**Mn**	**Cr**	**Mo**	**P**	**S**	**Ni**	**Fe**
Compositions (wt. %)	35CrMo	0.32	0.26	0.56	0.92	0.16	-	-	-	Balance

Table 3. Conditions used for corrosion tests

Run No.	**Sample**	**Pressure (MPa)**	**Exposure time(h)**	**Temperature (℃)**	**Corrosion medium**
1	35CrMo	9	24	120	Flue gas
2	35CrMo	9	48	120	Flue gas
3	35CrMo	9	72	120	Flue gas
4	35CrMo	9	96	120	Flue gas
5	35CrMo	9	24	150	Flue gas
6	35CrMo	9	48	150	Flue gas

7	35CrMo	9	72	150	Flue gas
8	35CrMo	9	96	150	Flue gas
9	35CrMo	9	24	200	Flue gas
10	35CrMo	9	48	200	Flue gas
11	35CrMo	9	72	200	Flue gas
12	35CrMo	9	96	200	Flue gas
13	35CrMo	9	24	250	Flue gas
14	35CrMo	9	48	250	Flue gas
15	35CrMo	9	72	250	Flue gas
16	35CrMo	9	96	250	Flue gas

3 Results and discussion

Experimental samples are morphologically analysed. The samples exposed at different temperatures at 9 MPa for 96 h were taken as examples to investigate the effect of temperature on the corrosion behaviours of alloy 35CrMo.

3.1 Increase in diffusion rate

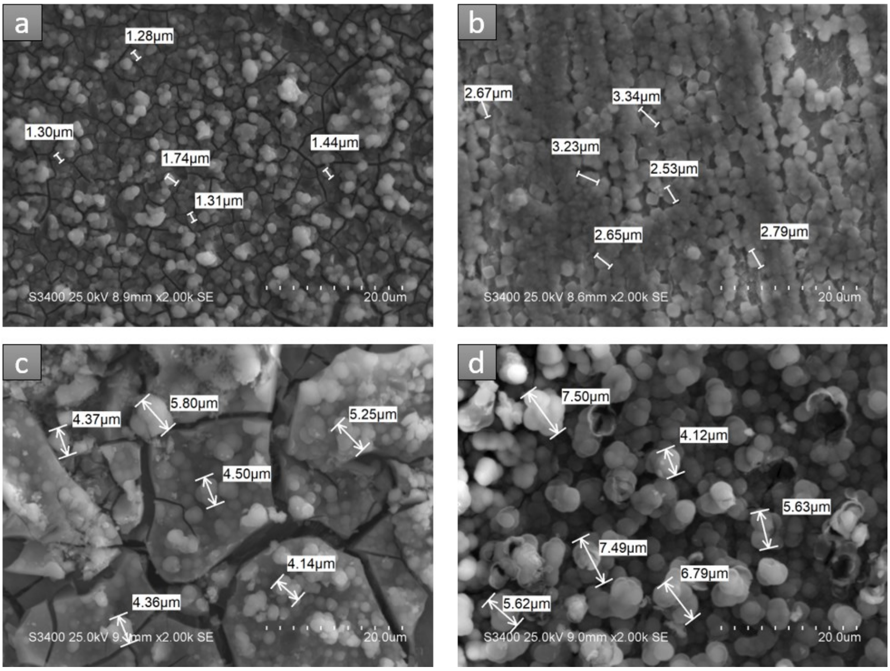

Fig. 1. Corrosion morphology of alloy 35CrMo exposed at (a) 120 °C, (b) 150 °C, (c) 200 °C and (d) 250 °C at 9 MPa for 96 h.

Fig. 1 shows varied corrosion morphology of alloy 35CrMo exposed at four different temperatures at 9 MPa for 96 h. According to Fig. 1(a), there are dense spherical oxides on the sample's surface after exposure at 120 °C for 96 h and no serious oxidation or dissolution is detected. At 150 °C, a continuous corrosion film has been found at the surface and the diameter of spherical oxide is larger than that at 120 °C. In Fig. 1(c), the oxidation film is thicker and the distance between cracks can be seen. With mean diameter changing from 4.74 μm at 200 °C to 6.19 μm at 250 °C, the phenomenon of larger spherical oxides and wider cracks appearing in Fig. 1(c) becomes more distinct in Fig. 1(d). The influence of moderate temperature range, represented by four distinct temperatures, is mainly reflected in the promotion of diffusion. It can be observed from the morphology that the size of spherical oxides and the thickness of oxide films are increasing with increasing temperature, which indicates that higher temperature can accelerate the diffusion rate of both alloy ions and corrosive gases.

3.2 Changes in the appearance of oxides

In addition to increase in diffusion, temperature can also affect the stability of oxides, which is reflected by the change of the morphology. At relatively high temperature, oxygen and solute change from lattice diffusion to grain boundary diffusion. Oxides are easy to precipitate and then grow up along the grain boundary, bringing on rod-like and lamellar structure. At higher temperature, iron ions and atoms directly spread out from the lattice, resulting in the emergence of larger spherical particles. Fig. 2 indicates the corrosion morphology of 35CrMo at 150 °C and 250 °C and both take on totally different oxidation appearance. At 150 °C, diffusion mostly happens in intergranular space, leading to the generation of needle-like oxides, which possess high density and strong corrosion resistance. On the contrary, the oxidation appearance of the right picture shows that oxides have turned to sphere.

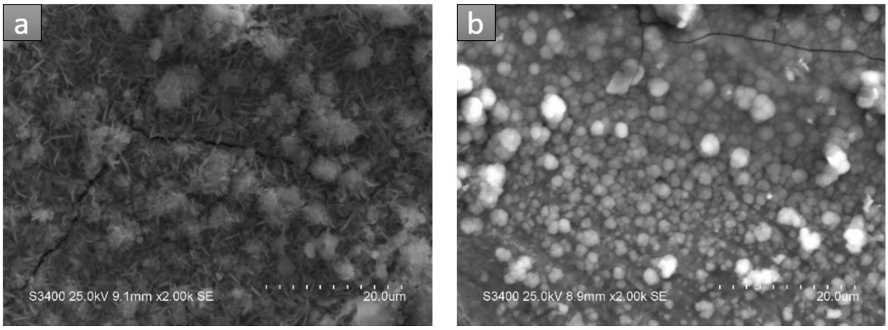

Fig. 2. Corrosion appearance of 35CrMo exposed at (a) 150 °C and (b) 250 °C at 9 MPa for 48 h

4 Conclusions

In this paper, after exposure in flue gas for 24 h, 48 h, 96 h and 120 h respectively, the effects of moderate temperature on alloy 35CrMo used for casing and pipeline in oil field are studied at same pressure and flue gas environment. Then, by using scanning electron microscopy (SEM), corrosion morphology analyses are achieved and main conclusions are listed as follows.

The typical corrosion behaviour of low temperature corrosion initiated by SO_2 and high temperature corrosion initiated by SO_2 and CO_2 did not appear at four chosen temperature points (120 °C, 150 °C, 200 °C and 250 °C). With the increase of temperature, the nucleation rate of oxide particles almost keeps constant, but the growth rate of oxide particles is accelerated, resulting in larger particle size. As we already mentioned in the increase in the diffusion rate, the diffusion activation energies of iron ions and atoms, oxygen ions in the matrix and oxides are diverse, and temperature is one of the key factors to satisfy the need of the diffusion activation energy of these elements. That is to say, the increase of temperature will improve the diffusion ability of iron ions and atoms and oxygen, so that the reactions take place that should not have happened.

Besides, temperature will affect the stability of oxides, and the consequences will be reflected on the morphology. At low temperature, oxygen and solute change from lattice diffusion to grain boundary diffusion. The oxides are easy to precipitate and grow up along the grain boundary, leading to rod-like and lamellar structures. At high temperature, the intensified diffusion of iron ions and atoms changes the appearance of oxides by resulting in bigger oxide particles and thicker oxide films, even the transmission from needle-like oxides to spherical oxides.

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