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## Study of corrosion process of 38CrMoAl in flue gas

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**Abstract.** The experiments were carried out on 38CrMoAl at 3MPa and 150 °C, which the temperature and pressure conditions were set to simulate the actual production conditions. The measurement methods included scanning electron microscopy analysis, X-ray energy diffraction spectrum analysis. The experimental results show that the corrosion of 38CrMoAl in the flue gas have a certain periodicity, and the corrosion process can be summarized as a cyclic process: oxidation-film formation-rupture-continuing oxidation. It can be inferred that as the exposure time increases, the corrosion process continues to circulate, and the cracking of the oxide film under the action of various stresses may even cause it to fall off, which would result in serious damage to the material.

### 1. Introduction

Secondary oil recovery is a kind of intensive development measure which is adopted to develop the nearly exhausted oil field by relying on the natural energy. Recently, flue gas assisted oil recovery has been widely applied in oil field as a secondary oil recovery technology, which aims to increase production and oil recovery. Meanwhile, as the specific application of CCUS (Carbon Capture, Utilization and Storage) technology, flue gas assisted oil recovery can fully capture, utilize and store a large amount of CO<sub>2</sub> gas generated by boilers <sup>[1]</sup>, which is conducive to environmental protection and generates good economic benefits. However, the corrosive gas (CO<sub>2</sub>, O<sub>2</sub>) in the flue gas is more corrosive to steel, which results in corrosion of oil well pipelines and even pitting.

For the corrosion of flue gas to steel, the current focus is mainly on the corrosion of the boiler system by the flue gas generated by boiler combustion. Some scholars have studied the high temperature flue gas corrosion under normal pressure <sup>[2,3]</sup>. However, in the flue gas assisted oil recovery process, the corrosion of the pipeline is different from the flue gas corrosion under normal pressure due to a higher pressure. At present, the corrosion of oil well pipe is mainly concentrated on CO<sub>2</sub> corrosion, and there are few studies on mixed flue gas <sup>[4]</sup>.

Hausler et al. <sup>[5]</sup> suggested that the corrosion reaction mechanism of bare metal and metal with surface film is different, and the mechanism of CO<sub>2</sub> corrosion is summarized as interface mechanism and phase mechanism. At present, most scholars have proposed a number of CO<sub>2</sub> corrosion reaction mechanisms based on the interphase mechanism, and no unified consensus has been formed. However, for the uniform corrosion in CO<sub>2</sub> corrosive media, the following unified conclusions are drawn: the corrosion rate and corrosion morphology are mainly determined by the flow rate and the corrosion product film <sup>[6]</sup>. Therefore, studying the corrosion process of carbon steel in flue gas is important.

The present paper aims to explain the corrosion process of pipeline material in flue gas assisted oil recovery through the simulation of the flue gas corrosion condition at 3MPa, 150°C for up to 96 h.



## 2. Apparatuses and procedures

### 2.1. Materials and apparatus

The material in this study was 38CrMoAl steel and the element contents are showed in table 1. The corrosion atmosphere (flue gas) was prepared according to the flue gas used in oilfield and the gas composition is shown in table 2.

The measurement methods included scanning electron microscopy analysis, X-ray energy diffraction spectrum analysis. The morphology of the metal surface was examined by a scanning electron microscope (SEM) instrument (JEOL 7800F). The element composition of the materials was identified by Oxford X-max Extreme energy diffraction spectrum (EDS).

**Table 1.** Element content of 38CrMoAl steel.

| Element | C     | Si    | Mn    | Cr    | Mo    | Al    | Fe  |
|---------|-------|-------|-------|-------|-------|-------|-----|
| Content | 0.33% | 0.30% | 0.38% | 1.45% | 0.19% | 0.97% | Bal |

**Table 2.** Gas composition of corrosion atmosphere.

| Composition | O <sub>2</sub> | N <sub>2</sub> | CO <sub>2</sub> | NO <sub>2</sub> | H <sub>2</sub> | H <sub>2</sub> S |
|-------------|----------------|----------------|-----------------|-----------------|----------------|------------------|
| Content     | 7%             | Bal            | 11%             | 0.005           | 0.001          | 0.001            |

### 2.2. Experimental procedures

All experiments were carried out in a high pressure tube reactor, which integrated flue gas inlet, PID control, solenoid valve automatic control pressure, temperature control. The tube reactor was made of superalloy GH1000 to withstand a maximum temperature and pressure of 1000°C and 30MPa, respectively. All materials were first buffed to 30mm by P-1 sample polishing machine.

The inner wall of the reactor was washed with deionized water to remove the deposits, and the tube was heated to 60°C for 10 min under unsealed conditions to ensure that the surface was completely dry. Then the materials were placed in the tube reactor through sample holder. The tube reactor was pressurized to 3MPa after purging for 10 minutes. When the pressure reached to the set point, all valves were closed and the heating program was started to 150°C. Furthermore, the temperature was dropped when reach to the setting time and the materials were taken after reaching their respective exposure time.

In order to explore the effects of exposure time, all materials were placed in the tubular reactor separately, and the corresponding exposure time was 24 h, 48 h, 72 h, 96 h, respectively. The specific experimental scheme is shown in table 3.

**Table 3.** Specific conditions of the experiments.

| Material | Pressure | Temperatur | Exposure time |
|----------|----------|------------|---------------|
| 38CrMoAl | 3MPa     | 150 °C     | 24 h          |
| 38CrMoAl | 3MPa     | 150 °C     | 48 h          |
| 38CrMoAl | 3MPa     | 150 °C     | 72 h          |
| 38CrMoAl | 3MPa     | 150 °C     | 96 h          |

## 3. Results and discussion

### 3.1. Analysis of corrosion surface morphology

The 38CrMoAl steel were conducted at 150°C, 3MPa within different exposure time. At different exposure time, the surface morphology of metal changed greatly, showing certain regularity.

**3.1.1. 24h exposure time.** Figure 1 shows the surface morphology on 38CrMoAl in 150°C, 3MPa after exposure in flue gas for 24 h. It is apparent from figure1 that after 24 h exposure, the material formed

spherical corrosion products in the smooth and clean layer, which still have clear scratches generated when polished. That is to say, the new corrosion products on the surface of the matrix was not formed a complete layer. At the same time, the energy spectrum analysis was performed on the surface particles and the region without covered particles. As shown in figure 2, the significantly different between the two areas indicated that the peak intensity of oxygen in surface particles was relatively stronger than the no-particle region, which proves that the spherical particle is the result of oxygen element enrichment.

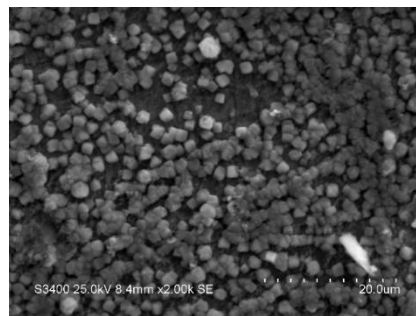


**Figure 1.** SEM images of the surface morphology on 38CrMoAl in 150°C, 3MPa for 24 h.

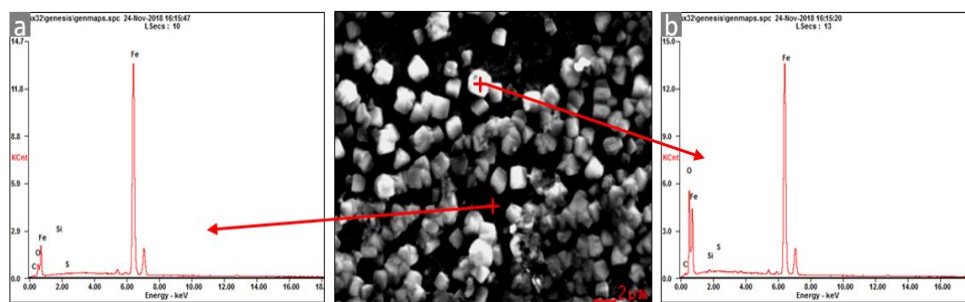


**Figure 2.** energy spectrum analysis of 38CrMoAl in 150°C, 3MPa for 24 h:(a) no-particle region; (b) particles.

**3.1.2. 48h exposure time.** Figure 3 shows the surface morphology on 38CrMoAl in 150°C, 3MPa for 48 hours. As shown in figure 3, obvious oxide particle stratification occurred on the surface of the 38CrMoAl steel after 48 h exposure. As the corrosion process progresses, a large amount of iron diffused outward while oxygen simultaneously enriched on the surface. Gradually, individual iron oxide balls were joined together by solid solution reaction to form a morphology as shown. The ratio of iron to oxygen was closer to 2:3, i.e., ferric oxide.

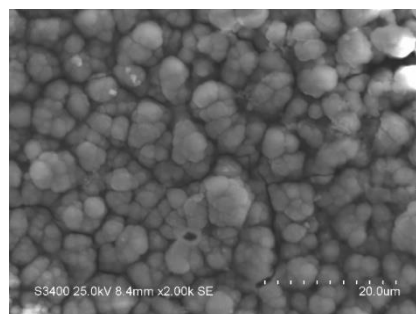


**Figure 3.** SEM images of the surface morphology on 38CrMoAl in 150°C, 3MPa for 48 h.

**3.1.3. 72h exposure time.** Figure 4 depicts the surface morphology on 38CrMoAl in 150°C, 3MPa for 24 h and 72 h. It is apparent that the ever-increasing spherical oxides on the alloy surface were mostly connected by solid solution reaction. However, the difference of iron diffusion velocity in different

regions of the matrix entailed the variance of the oxide particle. At the same time, the oxide connected into a piece, and formed cracks under the action of various stresses caused by the extrusion of corrosion products and the fluctuation of temperature and pressure, which was very unfavourable to the corrosion resistance of the material.

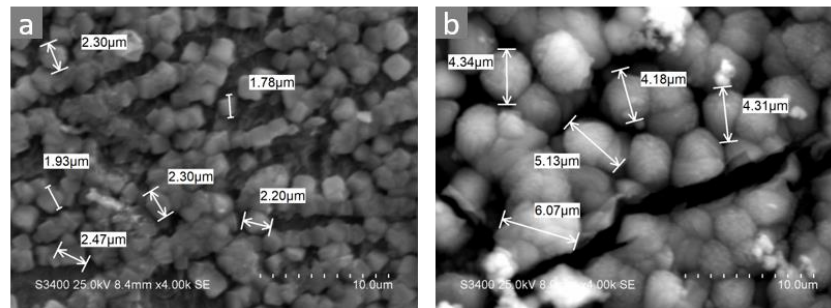


**Figure 4.** Surface particle size comparison of 38CrMoAl in 150°C, 3MPa: (a)for 24h (b)for 72 h.

**3.1.4. 96h exposure time.** Figure 5 shows the surface morphology on 38CrMoAl in 150°C, 3MPa for 48 hours. As the corrosion process continues, the iron diffusing continuously from the cracks in figure4(b) to the surface react with the oxygen to form new corrosion products. As shown in figure5, it could be seen that with the continuous corrosion and dissolution, the particle corrosion products on the surface gradually disappeared and became more flat. The outward diffusion of iron through the crevices and the reaction with oxygen resulted in the continuous thickening of the corrosion layer and the large fractured oxide layer.

As the high-pressure gas environment promoted the gas diffusion rate to the corrosion layer, the corrosion layer appeared obvious fracture to maintain the internal and external pressure difference, which indicated that the material had poor corrosion resistance in this corrosion atmosphere. The occurrence of oxidation, filming, fracture, continuous oxidation cyclic oxidation process is dangerous for the materials.

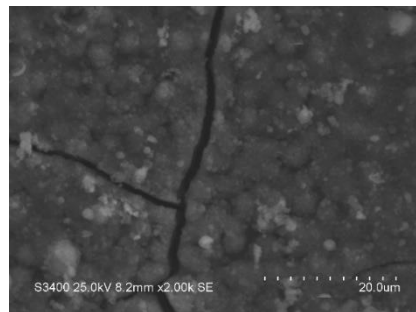


**Figure 5.** SEM images of the surface morphology on 38CrMoAl in 150°C, 3MPa for 96 h.

### 3.2. Corrosion mechanism in high pressure and temperature flue gas

**3.2.1. Crystal structure of corrosion products.** The main component of 38CrMoAl is iron, and EDS analysis under four exposure time showed that most of the corrosion products contained iron and oxygen. Therefore, the high temperature oxidation corrosion mechanism of 38CrMoAl can be mainly regarded as the high temperature oxidation process of iron.

When iron is oxidized in the flue gas at the experimental temperature of 150°C, it will grow into a rust layer containing  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$ , wherein  $\text{Fe}_3\text{O}_4$  is close to the metal. The  $\text{Fe}_3\text{O}_4$  phase is an inverse spinel structure in which half of  $\text{Fe}^{3+}$  is in the tetrahedral interstices, while  $\text{Fe}^{2+}$  and the remaining  $\text{Fe}^{3+}$  are in the octahedral interstices. Consequently, iron ions can diffuse through the defects at the octahedral and tetrahedral positions, which exhibits a certain degree of intrinsic

semiconductor characteristics and inevitably cause electrons to diffuse out into the conduction band through electron holes, just like excess electrons.

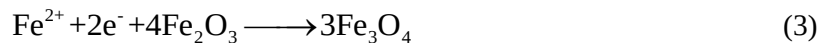
The  $\text{Fe}_2\text{O}_3$  phase has two forms: rhombohedral structure for  $\alpha\text{-Fe}_2\text{O}_3$  and cubic structure for  $\gamma\text{-Fe}_2\text{O}_3$ . Besides, though  $\text{Fe}_3\text{O}_4$  is oxidized to form  $\alpha\text{-Fe}_2\text{O}_3$  above  $400^\circ\text{C}$ , the presence of  $\text{Fe}_3\text{O}_4$  also needs to be considered due to the relatively low experimental temperature. In the rhombohedral structure, the combination between oxygen ions and iron ions in a gap position has the closed-packed hexagonal structure, which indicated iron ions were easily migrated.

**3.2.2. Physical diffusion process and chemical reaction equation.** Through the observation of the morphology of this experiment, the corrosion of most samples is mainly based on the formation of spherical corrosion particles on the surface. Therefore, it should not be the internal oxidation process caused by the inward migration of oxygen ions, but the surface oxidation process by the outward of the iron ions. The diffusion of iron ions is dominant in the oxidation process of iron based on the above introduction. Thus, the concise mechanism for the oxidation process of iron is as follows.

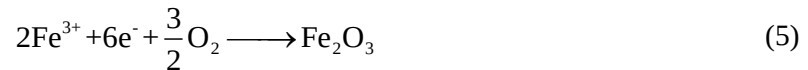
Iron ionized at the interface between iron and  $\text{Fe}_3\text{O}_4$ :



Iron ions and electrons diffused and migrated through the  $\text{Fe}_3\text{O}_4$  layer, which went by the iron vacancies and electron holes on the tetrahedron and octahedron respectively. At the interface between  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$ , the reactions of  $\text{Fe}_2\text{O}_3$  with iron ions and electrons formed  $\text{Fe}_3\text{O}_4$ :



In the  $\text{Fe}_2\text{O}_3$  layer, the outward migration of iron ions through vacancies together with electrons formed new  $\text{Fe}_2\text{O}_3$  at the  $\text{Fe}_2\text{O}_3/\text{gas}$  interface.



### 3.3. Corrosion process analysis

The corrosion model in flue gas was based on the outward diffusion of iron ions in dominant position. Figure 6 presents the schematic of the corrosion process. In the figure6, the corrosion process can be summarized as follows.

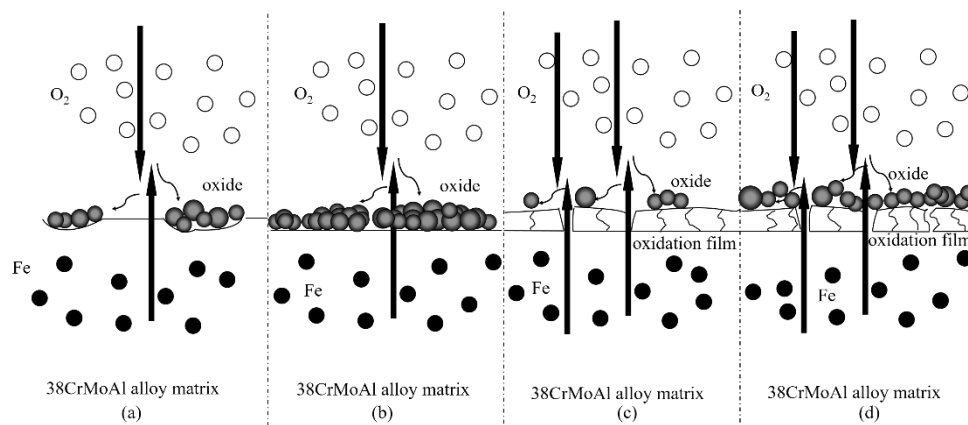


**Figure 6.** Schematic of the corrosion process.

First, iron ions in carbon steel matrix diffused outward while oxygen diffused inwards by ionization and adsorption on the surface of matrix, thus the contact between them on the surface of material form the spherical granular oxides. The EDS analysis of the surface particles and the uncovered substrate region showed that the oxygen content of the spherical particles was significantly

higher than that of the matrix region, which proved that the spherical particles were the result of oxygen enrichment.

Second, oxygen was constantly adsorbed on the surface and reacted with iron ions which were continuously diffused from the matrix. The size of the surface oxide particles increased to form the first oxide layer by becoming a piece, in which individual iron oxide particles were connected together at this step.

Third, the surface became more flat as the continuous corrosion and dissolution reactions caused spherical particles gradually disappear. The oxide layer ruptured under the influence of various stress such as temperature stress. Due to the diffusion of iron ions from oxide layer cracks and reaction with oxygen, the size of the surface oxide particles increased further.

Last, the protectiveness of first iron oxide layer was weak due to the generation of cracks. The outward diffusion of iron through the crevices and the reaction with oxygen resulted in the continuous thickening of the corrosion layer and the forming of large fractured oxide layer.

#### 4. Conclusions

In this work, experiment on 38CrMoAl steel was conducted to explain the corrosion process during the technology of flue gas assisted oil recovery. Experimental results indicated that the material exhibits a corrosion mechanism that iron oxide films grow periodically in high temperature and pressure flue gas. After continuous observation of 24 h, 48 h, 72 h, 96 h, the processes are concluded as a cyclic process: oxidation, film formation, rupture, continuing oxidation, which would cause relatively serious damage to the material.

#### Acknowledgement

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