Corrosion behaviour study of heat-resistant steel under oxidation and reduction atmosphere

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Abstract. High-temperature corrosion is one of the main problems that plague the safe operation of thermal power plants. Especially for units burning high-sulfur coal, the probability of high-temperature corrosion is much greater than that of units burning low-sulfur coal. In this paper, the 12Cr1MoV steel used in power plants is selected as the research object, the experiment studied the corrosion behavior of H₂S, SO₂ and air in the temperature range of 400-500°C. We found that 12Cr1MoV has the highest corrosion rate in the H₂S atmosphere, the second in the air, and the slowest in the SO₂ atmosphere.

1. Introduction

With the tightening of environmental emission standards, more and more thermal power plants have implemented ultra-low emission standards and strictly controlled nitrogen dioxide emissions below 50 mg/m³. The large power station boiler with subcritical parameters have higher temperature of water wall. The application of low NOx staged combustion technology makes the main combustion area in a lean oxygen state, and the reducing atmosphere near the surface of the water wall is more intense, which leads to high-temperature corrosion and thinning of the water wall tube. Once it is operated for a long time, it will cause steam leakage accidents in the pipe, leading abnormal shutdowns of the unit, bringing economic losses to the power generation enterprise, and threatening the safe operation of the power grid.

In terms of mechanism research, Cain [1] pointed out that alkaline metal trisulfate needs to be formed in an environment of at least 250 ppm SO₃. Nalson [2] found that the mixture of trisulfate compounds of alkali metals such as Na, K has a melting temperature lower than that of the pure substance, and can even be as low as 477°C. Hedly et al. [3] pointed out that SO₃ has insufficient retention time due to the reaction in the furnace, so the conversion rate is between 1.5 and 2%, and it hardly exceeds this range. Krause et al. [4] clearly indicated that the evidence for the formation of alkaline trisulfate compounds by SO₃ (1.5~2%) at this concentration is insufficient. Schofield [5] proposed a new method for reducing the high-temperature corrosion of sulfur and chlorine deposits using tungsten salts during combustion. Latham [6] proved through experiments that there is a good coupling relationship between chlorine and alkali metals. Krause [7-9] proved through experiments that the chemical corrosion of Cl₂ began at about 204°C, and the melting point of FeCl₂ is very low, which is a volatile substance. However, Cl₂ will cause severe corrosion to the metal only when the metal temperature reaches above 508°C. Lee [10] pointed out that FeCl₂ has a specific volume...
equivalent to about 11 times the reaction metal, so it is easy to lead to a porous permeable oxide layer with no protective properties. Brooks [11] found through experiments that chlorine is one of the important factors for the destruction of the oxidation protective layer on the wall of water-cooled tubes. Gibb [12] proposed that the chlorine content of coal not exceeding 0.3% is a method for selecting coal to avoid corrosion of chlorine. A. Hernas et al. [13] studied the high-temperature corrosion mechanism of 2.25% Cr–18% Cr series power station boiler heat-resistant alloy steel by simulating the oxidizing atmosphere of chlorine-sulfur. The results show that the corrosion resistance of heat-resistant alloy steel Sex determines the Cr content in the steel. Although there have been many researches on high-temperature corrosion mechanism and some progress has been made, there is no consensus on the corrosion mechanism. Based on this, this paper selects 12Cr1MoV pipe as the research object and experimentally studied in H₂S and SO₂. The corrosion rate under two corrosive atmospheres was analyzed.

2. Experimental devices
The whole system includes three parts: a gas distribution device, a reaction device and an exhaust gas treatment device. The gas distribution device is composed of a gas cylinder, a mass flow meter, a gas mixing device and a pipeline, and the gas is controlled by the mass flow meter and then mixed into the reaction device. The reaction device is an electric heating tube furnace with a temperature control error of ±1℃, a maximum heating rate of 25℃/min, and a maximum operating temperature of 1400℃. The furnace is a quartz tube with an inner diameter of 50 mm. The sample is placed in a constant temperature section of the furnace at a low temperature, filled with an inert gas, then heated to a reaction temperature and then thermostated, and the reaction gas is introduced into the reaction with the sample. After a predetermined time of reaction, the inert gas is charged and cooled, and the sample is taken out for detection. The exhaust gas treatment system is a gas filtration system containing NaOH, which absorbs harmful gases remaining after the reaction.

| Material  | C     | Si    | Mn    | Cr    | Mo    | V     |
|-----------|-------|-------|-------|-------|-------|-------|
| 12Cr1MoV  | 0.08–0.15 | 0.17–0.37 | 0.4–0.7 | 0.9–1.2 | 0.25–0.35 | 0.15–0.3 |

For better measurement, cleaning and processing and to weaken the influence of "border effect", the test pieces are machined by wire cutting with a size of 10 mm × 10 mm × 2 mm and with an accuracy of 0.001 mm in the test. The cut test pieces were smoothed with 800-mesh sandpaper, degreased with an anhydrous ethanol solution, and then blotted dry with a filter paper. After wrapping the clean paper, it is placed in a drying oven at 70℃ and dried at a constant temperature for use. The exact dimensions of the specimen were measured using a vernier caliper.

3. Experimental results and discussion

3.1. Corrosion rate in the air atmosphere
In order to characterize the corrosion rate under different working conditions, the unit time is defined, and the corrosion weight per unit area is the corrosion rate. Figure 1 shows the results of corrosion experiments of 12Cr1MoV under air atmosphere, in which the vertical axis on the left is the weight per unit area and the horizontal axis is the corrosion time. Considering that the sub-critical boiler water wall temperature is in the range of 400-540℃, the temperature conditions of the experiment in this paper are also selected in this range, as close as possible to the actual working conditions on site. It can be seen that at the three temperatures of 400, 450, 500℃, as the corrosion time increases, the weight gain per unit area increases at the beginning, and the subsequent increase is gentle, showing a parabolic growth law. Moreover, the higher the temperature, the bigger the corrosion gain. At the 168h corrosion time, the corrosion weight gain per unit area at 400℃ is 1.2 mg·cm⁻², and the corresponding
value at 500℃ is 4.8 mg·cm⁻², which is 4 times the corresponding value of 400℃. To further quantitatively describe the relationship between corrosion rate and corrosion time, the unit weight is squared to obtain a quantitative relationship model at three temperatures, as shown in the Figure 1.

The unit weight gain squared $y^2$ and the corrosion time $h$ show a good linear relationship. The quantitative relationship model at three temperatures is shown in Table 2. The correlation coefficient $R^2$ is above 0.98. The slope of the fitted line can reflect the magnitude of the corrosion rate.

**Table 2.** The relationship between the square area weight gain $y^2$ and the corrosion time $h$ at three temperatures.

| Temperature | 400℃  | 450℃  | 500℃  |
|-------------|-------|-------|-------|
| Air         | $y^2 = 0.01152t - 0.02568$ | $y^2 = 0.0403t - 0.1889$ | $y^2 = 0.1321t - 0.52083$ |
|             | $R^2 = 0.9882$             | $R^2 = 0.9944$             | $R^2 = 0.9977$             |

**Figure 1.** Corrosion experiment of 12Cr1MoV in the air atmosphere.

### 3.2. Corrosion rate in the H₂S atmosphere

Using the above data processing method, the relationship between the square of weight gain per unit area $y^2$ and the corrosion time $h$ under different concentrations of H₂S atmosphere can be obtained, as shown in Figure 2. Since the slope of the fitted straight line representing the corrosion rate, it can be seen that the higher the temperature, the greater the corrosion rate. Under the same temperature condition, the corrosion rate increases significantly with the increase of H₂S concentration. Taking 400℃ as an example, the slope of the fitted line of 0.02% H₂S atmosphere is 0.04, while the slope of the fitted line of 0.1% H₂S atmosphere is 0.44, which is 11 times that of the former. Moreover, comparing all the four kinds of H₂S atmospheres with the air atmosphere, the corrosion rate in the H₂S atmosphere is significantly faster. Taking the 400℃ operating condition as an example, the slope of air atmosphere fitting linear is 0.01, and the slope of 0.02% H₂S atmosphere fitting linear is it’s 4 times.
3.3. Corrosion rate in the SO$_2$ atmosphere

Similarly, using the above data processing method, the relationship between the square of weight gain per unit area $y^2$ and the corrosion time $h$ under different concentrations of SO$_2$ atmosphere can be obtained, as shown in Figure 3: the higher the temperature, the greater the corrosion rate. At the same condition of temperature, the corrosion rate increases significantly with the increase of SO$_2$ concentration. Taking 500℃ as an example, the slope of 0.02% SO$_2$ atmosphere fitting linear is 0.03, while the slope of 0.1% SO$_2$ atmosphere fitting linear is 0.07, which is 2.3 times of the former. In addition, comparing all the four kinds of SO$_2$ atmospheres with the air atmosphere, the corrosion rate under the SO$_2$ atmosphere is smaller than the corrosion rate under the air atmosphere. Similarly, taken the 500℃ operating condition as an example, the slope of the air atmosphere fitting line is 0.13, which is 4.3 times as the slope of the fitted line of the 0.02% SO$_2$ atmosphere.
4. Corrosion product morphology and composition of 12Cr1MoV

In order to reveal the microscopic mechanism of corrosion, the etched test piece was observed by a scanning electron microscope with an energy spectrum analyzer, and the surface topography of 10,000 times by SEM was shown in Figure 4.

4.1. Effect of temperature on the morphology of corrosion products

Figure 4(a) (d), (b) (e), (c) (f) are the surface topographies of the products after corrosion at different temperatures (400 and 500°C) in three atmospheres (Air, 0.08% H₂S and 0.05% H₂S). By comparing the two morphologies in the group, it can be seen that at 400°C, a rough undulating oxide film covers the three groups of surfaces, and the needle-like or feather-like crystals are interwoven into a network. These non-protective oxide films cannot prevent further corrosion. However, the surface crystal at 500°C is coarser and flakier. Compared with 400°C, it becomes porous, indicating that the corrosion is more intense, and the corrosive medium can be further corroded through the pores, especially in the H₂S atmosphere. The surface crystals are staggered and ruptured, and the laminates are convex and have a clear tendency to fall off.
4.2. Effect of atmosphere on the morphology of corrosion products

Figure 4(b) (c), (e) (f), (i) (j) are the surface topography of the products after corrosion at the same temperature and different concentrations of H$_2$S. It can be seen from the comparison that as the concentration of H$_2$S increases, the surface of the oxide film changes from needle-like to feather-like and lamellar. The volume of the crystal is getting larger while the cracks and the pores are getting denser, and the boundaries between crystals are getting blurred than before, indicating that the corrosion is intensified and the protection ability of the oxide film is decreased.

Figure 4(g), (h) are the surface topographies of the products after corrosion at different concentration of SO$_2$ at the same temperature. We can see from the comparison that a large number of fine needle crystals in the 0.02% SO$_2$ condition covers the surface, but the surface is flat and dense,
which can effectively prevent further corrosion. While in the 0.1% SO₂ condition, most of the surface is still made of dense needles, but some of the crystals grow significantly thicker and protrude from the surface, which destroys the overall compactness of the oxide film and thus reduces the corrosion resistance.

Figure 4(a), (b) and (h) are the surface topographies of conditions that 168h at 400°C under air, 84h at 400°C under 0.05% H₂S and 84h at 450°C under 0.1% SO₂. Since the corrosive medium content, temperature and corrosion time are not uniform, it can not be compared in a strict sense, but the general trend can be seen: a dense oxide film composed of fine needles under air, and a coarse overlapping feather or lamellar crystals under H₂S atmosphere, and very fine needle-like crystals under SO₂ atmosphere. Even if a small portion of the dense oxide film is destroyed at a higher SO₂ concentration, so it can be inferred that the oxide film protection in the test atmosphere is SO₂ atmosphere>air>H₂S atmosphere. While the oxygen content in the air is much higher than the SO₂ and H₂S contents in the test atmosphere, the corrosion capacity at the same concentration is H₂S>SO₂>O₂.

4.3. Surface composition of corrosion products

In order to qualitatively analyze the test results, an energy spectrum analysis test was carried out using an equipped X-ray energy spectrometer (EDS) while performing a scanning electron microscope SEM test. The surface element distribution of the sample after corrosion is shown in Table 3. Because the corrosive medium mainly contains S and O, and the metal substrate mainly contains Fe, Cr, Mo, and V, therefore focus is to observe the content of these elements.

| Elements | O     | Fe    | Cr    | Mo    | V     | S     |
|----------|-------|-------|-------|-------|-------|-------|
| Units    | at.% | wt.%  | at.% | wt.%  | at.% | wt.%  | at.% | wt.%  | at.% | wt.%  |
| 400°C Air| 60.9  | 30.48 | 37.95 | 66.31 | 0    | 0.24  | 1    | 2.94  | 0    | 0.03  |
| 500°C Air| 62.03 | 31.81 | 37.68 | 67.45 | 0.13 | 0.17  | 0.18 | 0.56  | 0    | 0     |
| 400°C 0.08%H₂S| 61.74 | 31.65 | 38   | 68.01 | 0.1  | 0.16  | 0    | 0     | 0.01 | 0.02  |
| 500°C 0.08%H₂S| 61.95 | 31.82 | 37.47 | 67.18 | 0.38 | 0.64  | 0.05 | 0.15  | 0.11 | 0.18  |
| 400°C 0.05%H₂S| 61.27 | 31.21 | 38.51 | 68.48 | 0.12 | 0.2   | 0.01 | 0.31  | 0    | 0     |
| 500°C 0.05%H₂S| 61.61 | 31.44 | 38.01 | 67.7  | 0.08 | 0.13  | 0.05 | 0.15  | 0.01 | 0.02  |
| 450°C 0.02%SO₂| 61.63 | 31.23 | 37.22 | 65.84 | 0.19 | 0.31  | 0.82 | 2.48  | 0    | 0     |
| 450°C 0.1%SO₂| 61.38 | 31.31 | 38.34 | 68.26 | 0.2  | 0.32  | 0    | 0.03  | 0.05 | 0.06  |
| 450°C 0.02%H₂S| 61.74 | 31.65 | 38   | 68.01 | 0.1  | 0.16  | 0    | 0     | 0.01 | 0.02  |
| 450°C 0.1%H₂S| 60.69 | 30.66 | 39.01 | 68.81 | 0.11 | 0.19  | 0.07 | 0.21  | 0.03 | 0.04  |

It can be seen from Table 3 that the surface of the product is mainly iron and oxygen, chromium, molybdenum and vanadium are all trace amounts, while the surface of the sulfur-containing atmosphere also contains trace amounts of S. From the table, it can be calculated that the proportion of Fe in the surface metal element is about 0.954–1 (see Table 4), while the mass content of iron in the 12Cr1MoV substrate is above 97%, so it is understandable that the surface metal element is mainly Fe.
The atomic ratio of M/O in metal M₃O₄ is 1.33, and the atomic ratio of M/O in metal M₂O₃ is 1.5. Calculating the atomic ratio of surface metal elements and non-metal elements (see Table 3), it is found that the (Fe+Cr+Mo+V)/(O+S) atomic ratio is about 1.55~1.63, and the Fe/O atomic ratio is about 1.59~1.66, even higher than M₂O₃. The difference may be the formation of higher-priced oxides such as MoO₂, MoO₃, V₂O₅, etc., may also be caused by measurement errors. Assuming that all elemental oxides take a high valence state, theoretically, the maximum number of O atoms is required to be 1.5Fe+1.5Cr+3Mo+2.5V. After calculating the atomic ratio O/(1.5Fe+1.5Cr+3Mo+2.5V), it is found to be greater than 1, which is not in accordance with common sense and can be determined as a measurement error. It can also be confirmed that the main component of the surface is Fe₂O₃, and a small amount of other metal oxides and the sulfur-containing atmosphere also contains trace amounts of sulfides.

It can be seen from Table 4 that there are some differences in the surface element content under different atmospheres and different temperatures, but the change is not large. Considering the existence of measurement error, it is difficult to distinguish the surface element content with the change of atmosphere and temperature. It can be considered to be substantially unchanged, and 95% or more of the surface component is Fe₂O₃.

| Element ratio | Fe | Fe + Cr + Mo + V | O | Fe + Cr + Mo + V |
|---------------|----|-----------------|---|-----------------|
| Units         |    | O + S           |    | O + S           |
| 400°C Air     | 0.9538 | 1.56 | 1.01 | 1.60 |
| 500°C Air     | 0.9893 | 1.63 | 1.08 | 1.65 |
| 400°C 0.08% H₂S | 0.9974 | 1.62 | 1.08 | 1.62 |
| 500°C 0.08% H₂S | 0.9858 | 1.63 | 1.08 | 1.65 |
| 400°C 0.05% H₂S | 0.9926 | 1.59 | 1.06 | 1.59 |
| 500°C 0.05% H₂S | 0.9956 | 1.62 | 1.08 | 1.62 |
| 450°C 0.02% SO₂ | 0.9593 | 1.62 | 1.05 | 1.66 |
| 450°C 0.1% SO₂ | 0.9946 | 1.59 | 1.06 | 1.60 |
| 450°C 0.02% H₂S | 0.9974 | 1.62 | 1.08 | 1.62 |
| 450°C 0.1% H₂S | 0.9936 | 1.55 | 1.03 | 1.56 |

5. Conclusions
The corrosion behavior of 12Cr1MoV steel under H₂S, SO₂ and air atmosphere at 400, 450, 500°C is systematically studied, and analyzed the high-temperature corrosion mechanism of gases in combination with corrosion topography. The main conclusions are as follows:

(1) It is found that the corrosion rate is highest in the H₂S atmosphere, and slowest in the SO₂ atmosphere. The corrosion rate is moderate in the air atmosphere. By analyzing the influence of temperature on the corrosion rate, it is found that the corrosion rate is roughly doubled for every 50°C interval at 400-500°C.

(2) The surface morphologies of 12Cr1MoV after corrosion were analyzed. It is a dense needle-shaped dense oxide film under air, a coarse porous oxide film composed of coarsely overlapping feathers or lamellar crystals under the H₂S atmosphere. Otherwise, under the SO₂ atmosphere, there exists a very dense and smooth oxide film composed of very fine needle-like crystals over the samples.
At higher SO₂ concentrations, some coarse feathery crystals appear on the surface. From the compactness, roughness and porosity of the oxide film, it can be inferred that the oxide film protection in the test atmosphere is SO₂ atmosphere > air > H₂S atmosphere. And since the oxygen content in the air is much higher than the SO₂ and H₂S content in the test atmosphere, Therefore, the corrosion capacity at the same concentration is H₂S > SO₂ > O₂.

(3) Comparing the surface topographies of 12Cr1MoV that after corrosion in the same atmosphere, it is found that the surface of 12Cr1MoV corrosion products is mainly Fe₂O₃. In addition, the higher the temperature and the concentration of the corrosive medium, the larger the crystal after corrosion, the coarser the surface, the greater the tendency of the oxide film to crack and peel, and the lower the corrosion resistance.

From the above, in the actual operation of the power plant boiler, the wall temperature and the concentration of H₂S near the wall should be strictly monitored to reduce the probability of high-temperature corrosion.

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