Study on the preventive Measures of Oxide Skin of 12Cr1MoV alloy steel Superheater

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Abstract. Through the analysis of the formation and structure of the oxide skin of 12Cr1MoV alloy steel, the formation mechanism of the oxide skin was studied, the causes and influencing factors of the oxide skin formation were obtained, and the measures to prevent the formation and fall off of the oxide skin of 12Cr1MoV superheater were put forward. The purpose of removing the oxide skin could be achieved by cleaning the formed oxide skin of the superheater.

1. Introduction
At present, the problem of boiler superheater tube explosion and shutdown caused by oxide skin falling off is quite prominent in power plants, and the accidents of boiler superheater tube explosion and shutdown caused by oxide skin falling off are common. Although some power plants do not cause shutdown, they also have a great impact on the safe and stable operation of the unit. In this paper, the causes and effects of oxide skin formation of 12Cr1MoV alloy steel superheater are studied through experiments. At the same time, it is proposed to clean the boiler superheater by chemical cleaning and remove the oxide skin in the superheater, which provides a guarantee for the safe and stable operation of the unit.

2. Study on oxide scale of 12Cr1MoV alloy steel

2.1. Scale formation of No.3 Boiler in a power plant
A thermal power plant was put into operation in 1997, with a capacity of 4 × 130t / h high pressure pulverized coal boiler and 2 × 25MW extraction condensing steam turbine unit.

During the minor repair of No.3 Boiler in the plant, it was found that there were black oxides at the bottom of the drum, the side of No.3 Boiler and No.4 boiler connecting door No.3 boiler. After that, the economizer, the four wall water wall, the lower header, the head at the bottom of the downcomer, the platen superheater and the high superheater were cut. It was found that the oxide skin in the superheater fell off seriously, and the inner wall of the economizer and the water wall tube was in good condition. Through the inspection and analysis of the turbine blades, it is found that the blades are scoured and damaged by particles.

The main pipe material of No.3 boiler superheater is 12Cr1MoVG. With the prolongation of the boiler operation time, the superheater will work under the condition of high temperature and high pressure water vapor medium for a long time, and there will be a series of problems such as tissue damage, creep damage and high temperature oxidation corrosion. In the boiler superheater, oxide skin will be formed gradually, and the oxide skin will fall off under certain conditions. The peeled oxide
skin will accumulate at the elbow of the superheater and cause the boiler tube to burst. Meanwhile, the peeled oxide skin will be brought into the steam turbine along with the steam, which will cause the solid particle erosion and damage the turbine blade. Therefore, it is very important to take effective measures to reduce the production and peeling of the oxide skin of the superheater and eliminate the influence of the oxide skin in the maintenance for the safe operation of the unit.

2.2. **Analysis of the current situation of the oxide skin of the superheater of boiler 3**

The 4 pipes of the cut pipe are the cold section pipe of the high temperature superheater and the hot section pipe of the high temperature superheater of the 3 boiler. See Table 1 for the number, sampling position, design material, operating temperature and other information of sampling pipe.

| number | Sampling location          | Texture of material | temperature °C |
|--------|----------------------------|---------------------|-----------------|
| 1      | Cold section of high temp  | 12Cr1MoVG           | 489             |
|        | superheater                |                     |                 |
| 2      | Cold section of high temp  | 12Cr1MoVG           | 489             |
|        | superheater                |                     |                 |
| 3      | Hot section of high temp   | 12Cr1MoVG           | 540             |
|        | superheater                |                     |                 |
| 4      | Hot section of high temp   | 12Cr1MoVG           | 540             |
|        | superheater                |                     |                 |

Table 2: Measurement results of inner wall oxide scale

| number | Thickness of oxide skin on inner wall |
|--------|---------------------------------------|
| 1      | 0.141mm                               |
| 2      | 0.103 mm                              |
| 3      | 0.097 mm                              |
| 4      | 0.124 mm                              |

Since the outer walls of the four sampling pipes submitted for inspection have been turned, only the thickness of the oxide skin on the inner wall can be measured. See Table 2 for the measurement results. The oxide skin on the inner wall of the cold forged and hot forged tubes of the high temperature superheater falls off seriously. The measurement result in Table 2 is the measurement value at the thickest part of the residual oxide skin. See Fig. 1-4 for the measurement.
2.3. Study on the formation mechanism of 12Cr1MoV oxide scale

Through the analysis of oxide skin, the following conclusions can be drawn: Fe₃O₄ and FeCr₂O₄ are the main oxides in the oxide film formed by 12Cr1MoV Steel in actual operation. FeCr₂O₄ has complex spinel structure and high compactness. It is difficult for the base metal to pass through the refractory and dense oxide layer, so the oxide layer has better protection.

The formation process of oxide film of 12Cr1MoV steel under the condition of high temperature and high pressure water vapor is described as follows:

Due to the outward diffusion of Cr, defects such as holes, cavities and microcracks will be formed in the formed Cr₂O₃ film; meanwhile, the oxide grain growth and plastic deformation will also generate micro channels conducive to the penetration of reactive materials. Water vapor penetrates the alloy / oxide interface through these defects in molecular form and reacts with the alloy. Due to the selective oxidation of Cr, there must be a Cr poor region at the alloy / oxide layer interface. When the water vapor molecules react with the Cr poor alloy, Fe₂O₃ will be generated. The reaction formula is as follows:

$$3H₂O+2Fe=Fe₂O₃+3H₂$$ (1)

The H₂ released by the reaction will form a local reducing atmosphere, which will make the Cr₂O₃ protective layer formed in the initial stage fail to reduce locally according to the following reaction formula.
\[3\text{H}_2 + \text{Cr}_2\text{O}_3 = 2\text{Cr} + 3\text{H}_2\text{O}\] (2)

The oxide of Fe formed by reaction (1) can form spinel FeCr\(_2\)O\(_4\) with the product Cr from reaction (2), and release H\(_2\), the equation is as follows:

\[\text{Fe}_2\text{O}_3 + 4\text{Cr} + 5\text{H}_2\text{O} = \text{FeCr}_2\text{O}_4 + 5\text{H}_2\] (3)

The oxides formed in 12Cr1MoV steel under the condition of high temperature and high pressure water vapor are Fe\(_3\)O\(_4\) and FeCr\(_2\)O\(_4\), both of which are spinel oxides of Me\(_3\)O\(_4\) type. According to this, the reaction equation of high temperature and high pressure water vapor oxidation of steel can be determined. The general formula is as follows:

\[3\text{Me} + 4\text{H}_2\text{O} \rightarrow \text{Me}_3\text{O}_4 + 8\text{H}\]

Oxidation film formed by oxidation of ferritic steel with high temperature water vapor. The inner layer of the oxide layer is called topotactischeschicht, and the outer layer is called epitaktischecht. It is formed by the outward diffusion of iron ions and the inward diffusion of oxygen ions in water. The inner primary membrane is the result of direct oxidation of iron by oxygen ions of water. The structure of iron oxide is Fe\(_2\)O\(_4\), Fe\(_3\)O\(_4\) or Fe\(_2\)O\(_3\), Fe\(_2\)O\(_3\) from the steel surface. The inner layer is of spinel fine particle structure, and the outer layer of oxide layer is of rod-shaped coarse particle structure with a certain amount of holes. As time goes on, there is a small amount of discontinuous Fe\(_2\)O\(_3\) in the outermost layer.

Under some unfavorable operating conditions (such as over temperature, temperature and pressure fluctuation), the double-layer film on the metal surface will become the structure of the multi-layer film, and then the oxidation and time will become a linear relationship. The bilayers first become two bilayers, then further develop into multilayer oxide structure of multiple bilayers, and then begin to peel off. The morphology of the multilayer film is shown in the figure below. Due to the alloy composition in steel, such as Cr, Mo, etc., when forming the double-layer film, the layer is very dense. The exfoliation of the oxide layer occurs in the middle of the two-layer film.

2.4. Study on peeling of oxide skin

There are two main conditions for oxide skin peeling: the first is that the scale layer reaches a certain thickness (critical value), generally speaking, 0.10 mm for austenitic stainless steel, 0.2-0.5 mm for chrome molybdenum steel, and it can be achieved after 20000-50000 hours of operation; the second is whether the stress (thermal stress caused by constant temperature growth stress or temperature drop) between the base metal matrix and oxide film or oxide film reaches the critical value (with the pipe, oxide film characteristics, and temperature change) The range, speed, frequency, etc. Theoretically, in order to peel off the water vapor oxide layer, the strain energy accumulated in the oxide film must reach or exceed the strain energy required for splitting along the weak part of the oxide film between the oxide film itself and the layer or between the oxide film and the base metal. When the thickness of oxide film thickens with the increase of running time, the strain energy required for its splitting becomes smaller, or with the increase of oxide film thickness, the more likely it is to peel off. One of the main sources of strain energy is the difference of thermal expansion coefficient between oxide film and alloy when the thickness of oxide layer reaches a certain value. When the temperature changes, especially when there are repeated or violent changes, the oxide skin is easy to peel from the metal body. For example, it has been found that the inner and outer layers of Cr Mo steel pipe are peeled off at the same time, and the thickness of the peeling off layer is usually more than 0.2mm, while the outer layer of stainless steel pipe is only 0.01-0.05mm. The oxide film of ferritic steel is much thicker when full thickness cracking or delamination cracking occurs.

As the formation of the oxide skin of superheater is inevitable, in order to minimize the harm of the oxidation belt of superheater, the oxidation-resistant alloy is generally used in China. The results show that the anti-oxidation and anti-corrosion properties of metal materials mainly depend on the formation of stable and compact oxide film on the metal surface. Due to the high cost, heavy workload and long cycle of pipe replacement, in order to avoid the peeling off of the oxide skin of the superheater, chemical cleaning can be adopted to clean the oxide skin in the superheater and avoid various risks caused by the peeling off of the oxide skin of the superheater.
Due to the disadvantages of high cost, heavy workload and long cycle of pipe replacement, in order to avoid the peeling off of the oxide skin of the superheater, chemical cleaning can be adopted to clean the oxide skin in the superheater and avoid various risks caused by the peeling off of the oxide skin of the superheater.

3. Measures to slow down oxidation and peeling of 12Cr1MoV alloy steel

3.1. Design
Use oxidation resistant alloy. The results show that the anti-oxidation and anti-corrosion properties of metal materials mainly depend on the formation of stable and compact oxide film on the metal surface. Cr2O3 is the only stable oxide in high temperature. The higher the Cr content enables the stronger the high temperature oxidation resistance of austenitic stainless steel. When the Cr content is higher than 20%, a dense protective oxide film Cr2O3 will be formed on the alloy surface. Generally, high chromium alloy steel can be considered when the unit is overhauled and replaced.

3.2. Operation, monitoring and maintenance
Improve boiler operation conditions, reduce steam overtemperature, reduce frequent unit start and stop, and reduce unit load fluctuation. Control the load rate of boiler to avoid frequent start and stop and reduce thermal shock. In the process of boiler shutdown, lower temperature drop rate shall be adopted as far as possible, and boiler cooling operation shall be strictly carried out. The furnace door shall be opened 12 hours after boiler shutdown.

It is believed that oxide stripping mainly occurs in the process of unit start-up and shutdown. Therefore, it can prevent the corrosion products from depositing in the superheater and reheater pipes to adopt fast start-up speed, strengthen the cold and hot water flushing before the unit starts, and strictly implement the shutdown and standby protection regulations of the unit. Long term furnace tube monitoring mechanism, including regular oxide skin measurement and wall temperature monitoring. Use the boiler shutdown opportunity to carry out radiographic inspection, confirm that the oxide layer debris at the bottom elbow of the vertical tube panel accumulates and cut the tube in time for cleaning. These measures can greatly reduce the production of oxide skin.

4. Study and application of chemical cleaning of oxide skin of 12Cr1MoV alloy steel

The scale will inevitably be produced in the unit superheater, and a large number of scale must be removed to ensure the safe and stable operation of the unit. At present, chemical cleaning method is widely used for removal.

4.1. Study on chemical cleaning of oxide skin of superheater
At present, the chemical cleaning of the oxide skin of the superheater in China is divided into two stages. In the 1970s and 1980s, most power plants used HF for chemical cleaning of the superheater. In the context of increasingly strict environmental protection policies, the use of HF acid is limited. At present, composite organic acid is mainly used for chemical cleaning of the superheater of the operating boiler.

The chemical cleaning of superheater is very difficult. First, the cleaning agent and cleaning aids should be selected to dissolve the oxide skin in the cleaning agent, so as to minimize the existence of insoluble oxide skin and the precipitation in the superheater elbow. The precipitated oxide skin will cause the tube explosion of superheater and the non-stop of the unit. Second, the proper cleaning flow rate should be selected to avoid the air plug in the tube, which will cause the air plug Some superheater pipes are not cleaned thoroughly, and the risk of oxide skin falling off still exists.

4.2. Screening test of scale cleaning agents and auxiliaries
One of the difficulties of chemical cleaning for the oxide skin of superheater lies in the selection of chemical cleaning agents and auxiliaries. Choosing the right cleaning agents and auxiliaries can fully
dissolve the oxide skin and be taken out of the boiler system by the cleaning solution, reducing the risk of oxide skin deposition. According to experience, cleaning agents are selected among hydroxyacetic acid, EDTA, formic acid, citric acid and sulfamic acid. The cleaning effect of single agent is not very ideal. Two or more agents are used in combination. After one month's dynamic simulation screening test, it is determined that the compound organic acid is the ideal drug HS-2 for cleaning. At the same time, the ideal inhibitor AD-5 is selected. In the test, the temperature is 90-98 ℃, and the mixed acid concentration is 6% for chemical cleaning.

By using the above cleaning formula, the chemical cleaning quality of the superheater of No.3 boiler has reached the standard of "DL / T 794" with excellent chemical cleaning quality index.

5. Conclusion
Through the above research, it can be concluded that the generation of oxide skin can be slowed down by appropriate methods, and the oxide skin can be removed by chemical cleaning.

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