Review of oxide scale on high temperature heating surface in boiler

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Abstract. The problem of oxide scale has always been a problem that hazards to the safe and stable operation of ultra-supercritical units, and is also the focus of equipment manufacturers, research institutes and production units. Therefore, the correct understanding and constructive result of investigation on the oxide scale’s origin, damages and formation has great guiding significance for the long-term operation of the unit.

Key words: oxide scale, ultra-supercritical unit, heat surfaces, boiler

1. Appearance and influence of oxide scale

Steel used for ultra-supercritical boiler is easy to be oxidized during operation as monitored. As early as 1929, German scientists discovered that metals can be oxidized in high temperature steam. The oxygen consumed in oxidation comes from the combined oxygen of steam itself, rather than the dissolved oxygen in steam[1]. Therefore, it is a natural process for steel surface (base material as well) to produce oxide scale in steam and the formation mechanism of oxide scale varies with the type of steel. Among them, temperature plays an important role in the growth rate of oxide scale, which is also the reason why the problem of oxide scale has gradually come into public view with the continuous improvement of steam parameters.

The consecutive growth and peeling of oxide scale will cause many problems, such as over temperature pipe burst, main steam valve jam, solid particle erosion of turbine blade and deterioration of steam water quality.
1.1. Over-temperature tube burst

After the oxide scale peeling off, the elbow under the heating surface will be blocked, which will lead to the decrease of steam flow and the over-temperature pipe burst. Due to the lack of understanding of the oxide scale problem, in a period of time shortly after the ultra-supercritical units were put into operation, the tube burst problems were relatively concentrated because of the oxide scale blockage, such as Guohua Taicang Power Plant, Huaneng Yuhuan Power Plant, Huaneng Qinbei Power Plant, Datang Chaozhou power plant, etc. The high temperature superheater was the most common location of tube burst, and the accidents covered different heating surface materials (T23, T91, tp34) 7h, etc.) and different manufacturers. Among them, 6 high temperature superheater tube burst accidents occurred continuously after 150000 hours of operation of No.2 unit of Shanghai Baogang Power Plant. Through inspection, the oxide scale in the pipeline has reached 0.8mm, and nearly 5T oxide scale has been removed by chemical cleaning. Therefore, it is a common problem that oxide scale formation endangers the safe operation of heating surface, especially high-temperature section in boiler.

The small particles of oxide scale will be taken away by steam flow, and larger particles will be deposited, resulting in blockage. At present, some power plants try to clear the oxide scale by means of quick opening and closing bypass during startup. Therefore, the migration law of oxide scale in pipeline is also an important direction in the research of oxide scale prevention and control. For solid particles, the main forces are steam drag force (caused by the relative velocity difference between particles and steam), basset force (caused by acceleration), rotational lift force (caused by self rotation of particles) and self particle gravity \[3\].

Through the analysis of the stress on particles and boundary conditions, the location of oxide scale in the pipeline can be predicted. The actual location distribution of oxide scale is consistent with the predicted results, especially at the outlet end, the scale accumulation is more serious.
1.2. Jamming of main steam valve
If the main steam valve can not be closed smoothly after the turbine is shut down, the runaway accident will occur at the moment of load rejection. If oxide scale enters the main steam valve of steam turbine, there exists the risk of erosion caused by jamming of main steam valve. Tieling power plant in 2009, the main steam valve and valve sleeve produced thick oxide skin. At present, large capacity steam turbine will carry out valve loosening test regularly to ensure that the valve has no jam during the whole stroke and eliminate the influence of oxide scale.

1.3. Solid particle erosion of blade
Oxide scale particles flow with steam at high speed, which causes mechanical damage of blade under impact and cutting, resulting in serious erosion of components of flow passage. This phenomenon will shorten the maintenance cycle, increase the maintenance cost and reduce the economy and safety of unit. EPRI of the United States has reported that the annual economic loss of the power industry due to solid particle erosion is up to 150 million US dollars.

1.4. Deterioration of steam water quality
The oxide scale will be further broken after impact with the turbine blade. The diameter of the oxide skin particles after crushing is between 5 ~ 50um. These particles can reach the place where the working fluid reaches, and become the source of thermal equipment sediment.

2. Ferrite and austenite steel
It is necessary to briefly introduce the substrate of oxide scale, that is, the type of heating surface material. At present, steel for high temperature heating surface is mainly divided into ferrite and austenitic steel.

Ferritic steel grades include T91, T92 and so on. Ferrite steel is characterized by good thermal conductivity and low coefficient of thermal expansion. At temperature of 450 ℃ and below, ferritic steel has good tensile strength; at higher temperature of 550 ℃, it has good creep resistance and excellent welding performance. At the same time, the price of ferrite steel is relatively cheap. The addition of alloying elements (Mo, Cr) can improve the creep resistance and steam oxidation resistance of ferritic steel, but when the steam temperature exceeds 620 ℃, the oxidation resistance of ferrite steel can not meet the operation requirements.
Austenitic steel is mainly developed from 18Cr8Ni, which can be divided into 15% Cr, 18% Cr and 20% - 25% Cr and high nickel and high chromium. Because of the high content of Cr and Ni, its high temperature comprehensive performance is better, so austenite TP347H becomes the substitute of T91, which is widely used in superheater pipe. The common austenitic steel grades are TP304H, Super304H, TP347H (TP347HFG) and HR3C. The thermal expansion coefficient of austenite is larger than that of ferrite steel, but the thermal conductivity is relatively small. When the steam temperature changes, thermal stress will be produced between different material parts of the boiler, which is more prone to produce fatigue cracks.

3. Morphology and formation of oxide scale

3.1. Morphology of oxide scale in ferrite and austenitic steel

In ferrite steel pipe, oxide scale with double layer structure is usually formed during high temperature oxidation. The outer oxide scale is mainly Fe$_3$O$_4$ (a small amount of Fe$_2$O$_3$) with columnar grain structure and defects such as pores and microcracks in the grain boundary region. The grain of inner oxide scale is axial. The content of Cr in the inner oxide scale depends on the Cr content of the matrix; the higher the Cr content in the alloy, the higher the Cr content in the inner oxide scale (the essence of the inner oxide scale is the mixed spinel composed of Fe and Cr).

![Fig. 3 Oxide scale cross section of ferritic steel][3]

![Fig. 4 Oxide scale structure on inner wall of TP347H (austenitic) pipe][4]

Because of the high content of Cr in austenite, Cr$_2$O$_3$ or Cr-Fe oxide will be formed in steam environment. The thickness of oxide skin on the inner wall of the tube is thin and the microstructure is fine. The oxide scale has a certain degree of erosion and oxidation to the metal matrix, which is characterized by concave and irregular oxide layer. The Cr rich oxide scale can effectively prevent the bidirectional diffusion of ions and improve the steam oxidation resistance of the metal. It can be seen from the figure that one layer near the metal matrix is Cr rich spinel structure, and the other layer is Fe rich magnet layer exposed to the steam side. The outer structure of the magnet layer is loose, and the inner spinel layer rich in Cr becomes the protective layer, which is firmly combined with the base metal to protect the matrix from being oxidized by steam. Therefore, the oxidation layer of austenitic steel is essentially a double-layer structure (also called three-layer structure in some literature).

At the same time, the metal grain size of austenitic steel has an important influence on the morphology of oxide film, which is because Cr element mainly diffuses along the grain boundary, and the fine grain is easier to promote the diffusion of Cr on the grain boundary, thus forming a dense
oxide film on the surface of austenitic steel, and the thickness of the oxide film is also thinner. The results show that the thickness of the oxide film of TP347HFG is only 1 / 3 of that of TP347H.

3.2. Formation of oxide scale

Oxidation mechanism of austenitic steel in supercritical water. Firstly, O$_2$ decomposed from H$_2$O or dissolved oxygen added into the environment is adsorbed on the metal surface, which is physical adsorption. Then these adsorbed O$_2$ molecules decompose, and oxygen atoms ionize into oxygen ions, which are chemically adsorbed. The electrons needed in these processes are provided by metals and diffuse through the oxide film to the oxide / supercritical water interface.

The initial reaction between chemically adsorbed oxygen ions and iron ions on the metal surface forms a thin layer of Fe-Cr oxide, which forms the activity gradient of oxygen at the oxide / matrix interface and oxide / supercritical water interface.

On the one hand, the Fe ions in the matrix diffuse along the oxide grain boundary or crystal under the driving of the oxygen potential gradient. On the other hand, oxygen diffuses from the oxide film / supercritical water interface mainly along the metal grain, and forms Fe-Cr-Ni oxide in the metal grain, and then oxygen surrounds the whole grain along the grain boundary and diffuses into the grain, so that the whole grain is oxidized to form Fe-Cr-Ni oxide It should be a mixture of FeCr$_2$O$_4$ and Fe$_3$O$_4$). The diffusion rate of Fe is much higher than that of Cr. Therefore, with the increase of oxidation time, the content of Cr diffused from grains to grain boundaries increases, while the content of Fe decreases. This results in the formation of Fe-Cr spinel (generally FeCr$_2$O$_4$) in the grain boundary near the oxide film / matrix interface. This is the reason why the layered structure of austenite oxide scale is formed.

4. Conclusion

Present study illuminates the origin of oxide scale in ultra-supercritical unit, and particularizes the risk of oxide scale on safe operation. Then two typical kinds of steel which are widely used in heating surfaces are introduced in order to figure out the difference of oxide scale layer formation. Last but not the least, the formation process is studied, though the detailed mechanism still needs to be investigated.

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