Analysis of Hydrogen Corrosion of Water Wall Tube of a Power Plant Boiler

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Abstract: During the operation of a power station boiler with the rated evaporation of 1025 t/h, its water wall tube, which is made of SA-210C, bursts continuously. Based on the fracture analysis, material inspection, metallographic examination, energy spectrum analysis and mechanical property analysis of the tube sample, this paper confirms that the cause of the water wall tube failure is hydrogen corrosion, which is accelerated by the copper impurity.

1. Introduction
The unplanned shutdown of units by the boiler in recent years caused is mainly due to the leakage of the heating surface. The water wall is located in the worst environment, making it the most possible to suffer from that problem [1]. Therefore, the effective analysis of the water wall leakage accident can provide guidance for the reliable operation of boiler.

The HG-1025/17.5-YM36 boiler of a power plant has a specification of Φ 63.5×7mm and is made of SA-210C. The internal medium of the water wall tube is a steam-water mixture at a temperature of 366 °C and under a pressure of 20.21 MPa. During its operation, leakage spots are generated on the fire side of the water wall tube with uneven corrosion pits.

2. Leakage spot test

2.1 Spot
The leakage spot on the water wall tube is on the fire side. The outer wall of the tube where the leakage spot locates is partially peeled off, and the outer wall of the fire side is dotted with brown marks. The inner wall of the leakage spot is shown in Figure 1. The inner walls of the back side and the fire side are evenly covered with a layer of sediment, while the inner wall of the fire side presents ulcer morphology. It can be seen that the color of the leakage spot is reddish brown and partially dark gray. A crack can also be clearly observed, as indicated by the red arrow. In addition, many water flow wash marks can be observed, as indicated by the yellow arrow. Figure 2 is a secondary electron mosaic of the inner wall of the leak spot at a lower magnification when the sample is observed under a scanning electron microscope. The energy spectrum analysis is performed in the 1~5 regions near the crack and the results are shown in Table 1.
According to Table 1, the oxygen content of each spot is relatively high and the copper content of spots 1 and 3 in Figure 2 is the highest. Spot 1 is located inside the crack, with a copper content of 50.88%, while spot 3 has a higher copper content of 80.13%, and the microscopic morphology is granular. According to the results of the energy spectrum analysis, the local copper content at the leakage spot is high, and there may be copper impurities.

2.2 Fracture observation
Two dual fractures can be obtained after opening the leakage spot along the crack. The minimum wall thickness of the fracture is 3.7 mm, while the wall thickness of the water wall tube is 7 mm, indicating the existence of significant corrosion reduction. Figure 3 is what can be observed after putting fracture 1 under a scanning electron microscope. Figure 4 is the secondary electron mosaic at a lower magnification. This paper observes in detail all parts on the fracture, and conducts energy spectrum analysis of the A–E regions. The results are listed in Table 2.
The fracture morphology is basically intergranular fracture. There are also oxidized particles, and the oxygen content is high. Element distribution result indicates the local aggregation of copper. Figure 19 shows the morphology of the spot C, where there are traces of water scouring and the oxygen content is high. Spot D is near the edge of the fracture and has an intergranular morphology. Spot E has morphology of granular, with a copper content as high as 82.22%, which should be copper impurity.

3. Test analysis

3.1 Metallographic observation
The metallographic structure of the fracture sample is shown in Figures 5 and 6. In Figure 5, the bright yellow copper impurity and a layer of gray-black iron oxide covering the fracture can be observed. Figure 6 is the metallographic structure of the inner wall near the fracture, which is basically ferrite with a large number of small cracks. It can be seen that all the cracks are along the grain boundary, and a few obvious ones are indicated by the red arrows.

Table 2. Energy spectrum analysis results of different parts of the fracture (wt, %)

|   | C   | Si  | Mn  | Fe   | Cu  | O   | Al  |
|---|-----|-----|-----|------|-----|-----|-----|
| A | 2.67| -   | 0.96| 89.00| -   | 7.38| -   |
| B | 5.65| -   | -   | 59.64| 19.75| 17.95| -   |
| C | 2.52| 0.33| -   | 81.83| 0.33| 14.45| 0.55|
| D | 2.91| 0.37| 0.83| 89.03| -   | 6.85| -   |
| E | 6.58| -   | 0.39| 4.46 | 82.22| 6.35| -   |
According to the above observation, the tissue away from the fracture is ferrite and pearlite; that on the inner wall near the fracture is mostly ferrite, and that on the outer wall is ferrite and pearlite. This indicates the existence of decarburization in the inner wall of the fracture. This paper puts the metallographic sample of Figure 5 under a scanning electron microscope to obtain the back-reflection electron image, which is shown Figure 7. It can be seen that there are a large number of small cracks near the inner wall, and the number of crack increases as it gets closer to the fracture. A boundary is formed between the inner and outer walls, as shown by the red dotted line. Divide the wall into A and B. Part A is close to the inner wall, with a lot of small cracks; Part B is close to the outer wall with almost no crack.

![Figure 7. Back reflection electron image of the fracture](image)

Based on the metallographic observation, it is found that the inner wall tissue at the fracture is decarburized, with a large number of small intergranular cracks.

### 3.2 Chemical component analysis

This paper takes a 30×30 mm sample on the back side of the water wall, and sands its surface for the chemical component analysis using direct-reading spectrometer. Through the comparison of the results in Table 3 with the ASME SA-210/SA-210M standard, it is found that all elements, except copper, are in compliance with the standard requirements [2].

|     | C   | Si  | Mn  | Cu  | P   | S   | Fe  |
|-----|-----|-----|-----|-----|-----|-----|-----|
| Measured value | 0.22 | 0.23 | 0.83 | 0.11 | 0.012 | 0.008 | remain |
| ASME A-210C | ≤ 0.35 | ≥0.1 | 0.29~1.06 | - | ≤ 0.035 | ≤ 0.035 | remain |

### 3.3 Tensile properties

Take and prepare three tensile specimens of the intact areas of both the fire side wall and the back-side wall of the tube for tensile test. The measured tensile properties are listed in Table 4. All properties meet the standard requirements, and the strength of the fire side is slightly lower than that of the back side. The microscopic topography of the tensile fracture is shown in Figures 36 and 37, which belongs to the dimple morphology.
Table 4. Mechanical properties of the material

| Tested area   | No. | Yield strength (MPa) | Tensile strength (MPa) | Elongation (%) |
|--------------|-----|---------------------|------------------------|----------------|
| Back side    | 1#  | 332                 | 568                    | 32.5           |
|              | 2#  | 350                 | 569                    | 32.5           |
|              | 3#  | 348                 | 566                    | 31.0           |
|              | Average | 343               | 568                    | 32.0           |
| Fire side    | 1#  | 329                 | 562                    | 32.0           |
|              | 2#  | 317                 | 552                    | 33.0           |
|              | 3#  | 333                 | 562                    | 32.5           |
|              | Average | 326               | 559                    | 32.5           |
| Standard specified value | ≥275 | ≥485 | ≥30 |

4. Result analysis

4.1 Result analysis
According to macroscopic observation, the leakage spot is on the fire side. The thickness of the inner wall of the fracture is significantly reduced, indicating that the leakage starts at the inner side of the fire side. Microscopic observation shows that most of the fracture surface is heavily oxidized and the slightly oxidized area is intergranular fracture, whose artificial fracture belongs to the dimple morphology. The energy spectrum analysis indicates the existence of copper impurity in the fracture. Metallographic examination shows: 1) The tissue of inner wall of the leakage spot is basically ferrite, and that of outer wall is ferrite and pearlite, indicating the existence of decarburization of the inner wall [3]. 2) There are many small intergranular cracks on the inner wall. 3) Divide the wall into A and B. Part A is close to the inner wall, with a lot of small cracks; Part B is close to the outer wall with almost no crack. Moreover, based on the trend of the boundary line between A and B (red dotted line in Figure 7), the number of crack increases as it gets closer to the fracture, indicating that more cracks are located in the thicker part. That phenomenon shows that the fracture is formed through the connection of intergranular cracks at high temperature and under high pressure.

The above results show that the failure starts at the inner wall of the fire side with the characteristic of decarburization at the fracture and a large number of intergranular cracks on the inner wall.

4.2 Hydrogen corrosion
Due to the complicated working environment, the water wall pipe of power station boilers often suffers from damages and failures which are caused by acid corrosion, high temperature corrosion, fatigue, wear, hydrogen corrosion, overheating, etc. [4]

Hydrogen corrosion is a form of high temperature damage caused by hydrogen damage, which happens to carbon steel or low alloy steel at a high temperature and under high pressure environment containing hydrogen for a long time. The source of hydrogen may be the hydrogen produced by steam corrosion, or the hydrogen released by the under-deposit acidic corrosion due to the low pH of the water and the concentration of acidic substances into the sediment [5]. Regardless of the source, if the hydrogen cannot be quickly taken away by water or steam, the atomic hydrogen will permeate into the interior of the metal to react with cementite at a certain temperature and pressure (for the carbon steel, the temperature shall be greater than 250 °C and the hydrogen partial pressure shall be greater than 2 MPa).

\[
\text{Fe}_3\text{C} + 4\text{H} \rightarrow 3\text{Fe} + \text{CH}_4 \uparrow
\]
On the one hand, this reaction decomposes cementite, leading to surface decarburization or internal decarburization. On the other hand, the generated CH4 molecules will accumulate on the impurity or grain boundaries to form CH4 bubbles, which will grow as CH4 continues to aggregate and finally form hydrogen corrosion cracks along the grain boundaries.

4.3 Comprehensive analysis
The water wall tube is made of high-quality carbon steel, which has the possibility of hydrogen corrosion. According to the analysis results, the failure is characterized by the decarburization at the fracture and a large number of intergranular cracks on the inner wall. These characteristics are completely consistent with those of hydrogen corrosion. Therefore, the leakage is estimated to be caused by hydrogen corrosion. Further, the wall gets thinner as it gets closer to the inner wall, which is also caused by hydrogen corrosion.

In addition, the material of the water wall tube is SC-210C, which should not contain copper according to the standard. However, the test result shows that it contains 0.11% copper. SEM and metallographic observation all prove the existence of copper impurity located at the fracture, which will make the internal structure of the material not loose and discontinuous. When hydrogen corrosion occurs, copper impurity will facilitate the accumulation of methane gas, making the tube more likely to fail.

5. Conclusion and recommendations
The direct cause of the water wall burst is hydrogen corrosion, and the indirect cause is the presence of copper impurity in the water wall that accelerates the corrosion. Therefore, it is necessary to strictly check the tube material during the installation process of power station boilers so as to avoid unplanned shutdown caused by unqualified materials. Secondly, it is important to ensure the water quality by implementing water quality inspection and chemical instrument calibration during the operation of the power station boiler. Thirdly, it is necessary to strengthen the anti-wear and explosion-proof inspection of the heating surface so as to eliminate potential safety hazards in time before accidents.

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