Failure Mechanism of Water Wall Coating Prepared by Supersonic Arc Spraying

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Abstract. In order to meet the requirements of environmental protection, low nitrogen combustion is widely used in thermal power plants, which causes serious high temperature corrosion of water wall on fire side. At present, some power plants use water wall anti-corrosion coating to improve their service life. In this paper, a power plant water wall coating off to explore, analysis of water wall corrosion mechanism and coating failure reasons. The results show that: The direct reason for the large-scale peeling off water wall coating is that S element penetrates through the pores of the coating and corrodes the coating, resulting in the decrease of the adhesion between the coating and the substrate and the generation of a large number of microcracks. The microcracks continue to expand and extend under the action of thermal stress and S corrosion, which eventually leads to the large-scale peeling off the coating.

Keywords. Water wall; high temperature corrosion; coating failure; S element; microcrack.

1. Introduction
With the national economic development of our country, the electricity consumption for production and living continues to increase, and thermal power units are also developing toward large capacity and high parameters. High temperature corrosion of boiler water walls has become one of the urgent problems for power generation enterprises to solve [1-3]. Using excellent high-temperature alloys can effectively improve the high-temperature corrosion resistance of the equipment, but it is cost-constrained during use due to its high price [4, 5]. Compressed air is used in supersonic arc spraying to atomize the molten wire and sprays it on the workpieces at supersonic speed to form a coating with high bonding strength, low porosity and low surface roughness [6-9], which can effectively improve high temperature corrosion resistance performance of the material with low cost. KM99 alloy wire is used as an arc spray powder core wire containing Cr, Ni, B and other alloys or ceramics. The coating formed by it is highly wear-resistant and corrosion-resistant for the amorphous phase coating contained. However, the KM99 coating of the water wall of a power plant was completely peeled off within a short operating time. In this paper, failure causes of the coating through related inspections are analyzed and corresponding suggestions to improve the quality and performance of the coating are made.
2. High Temperature Corrosion Mechanism

The main cause of high temperature sulfur corrosion of the boiler water wall is the oxygen-deficient operation of the main combustion zone caused by the low-nitrogen combustion of the ultra-low emission boiler. The pyrite (FeS$_2$) in the pulverized coal is burned and heated to decompose free sulfur:

$$\text{FeS}_2 \rightarrow \text{FeS} + \text{S}$$  \hspace{1cm} (1)

At the same time, the H$_2$S present in the flue gas reacts with SO$_2$ and O$_2$, free sulfur atoms released:

$$2\text{H}_2\text{S} + \text{SO}_2 \rightarrow 2\text{H}_2\text{O} + 3\text{S}$$  \hspace{1cm} (2)

$$2\text{H}_2\text{S} + \text{O}_2 \rightarrow 2\text{H}_2\text{O} + 2\text{S}$$  \hspace{1cm} (3)

When the wall temperature reaches 350°C,

$$\text{Fe} + \text{S} \rightarrow \text{FeS}$$  \hspace{1cm} (4)

By direct penetration, S reacts directly with Fe through the sealant, vulcanizes the Fe inside, and heavy high-temperature corrosion happens. S$^2-$ has strong reducibility, thus it can remain stable in reducing gas. However, the oxidizing gas slowly oxidized into Fe$_3$O$_4$, when the pressure of gas in the flue gas reaches a certain partial value. The SO$_2$ generated by the reaction increases the activity of atomic sulfur and accelerates the corrosion of the metal, making the corrosion worse [1-3].

$$3\text{FeS} + 5\text{O}_2 \rightarrow \text{Fe}_3\text{O}_4 + 3\text{SO}_2$$  \hspace{1cm} (5)

Cr is sulfided before Fe, Ni and other metal elements. During the sulfidation process, a dense layer of Cr sulfide is formed on the surface of the alloy. Cr has fewer sulfide crystal defects. The formation of a complete and uniform chromium sulfide layer can block the outward diffusion of metal ions and the penetration of S into the alloy matrixe, which greatly reduces the corrosion rate [6-11]. Less Cr element in the wire area of KM-99, a dense vulcanized layer cannot be formed. The wire cannot prevent S from penetrating into the substrate, causing high temperature corrosion of the coating and the substrate.

3. Test Analysis

One 600MW unit of a power plant has serviced for about 50,000 hours of operation. KM-99 wire was used for supersonic arc spraying on boiler water wall tube (design specification φ32×8mm, design material 15CrMoG) of the unit, and CT-F ceramic micro-powder sealant was used to seal the holes. Large scale peeling off the water wall coating was found after about another 7000 hours running of the unit (average wall temperature was 375°C). The morphology features of the coating and its attached corrosion products was observed by scanning electron microscope (SEM), and energy spectrometer (EDS) was used together with back-scattered electron imaging to measure the composition of the remaining coating and the surface corrosion products on its surface.

3.1. SEM Analysis

Scanning electron microscope (SEM) was used to observe the morphology features of the coating and its corrosion products attached. Figures 1 and 2 show the SEM morphology of the normal area of the water wall coating. The left area is the coating, and the right area is the base metal. The coating and the substrate are tightly bonded, no cracks are found.
Figure 1. SEM morphology 1 of normal area of water wall coating.
Note: Chinese characters (谱图 1-7) in figure mean points of energy spectrum 1-7.

Figure 2. SEM morphology 2 of normal area of water wall coating.
Note: Chinese characters (谱图 8-11) in figure mean points of energy spectrum 8-11.

Figure 3 shows the macroscopic morphology of the peel-off area of the water wall. The surface coating of the water wall has been basically peeled off, only a small amount of coating remaining. On the surface of the substrate where the coating peeled off are evident signs of corrosion (the white arrow refers to the remaining coating).
Figure 3. Macroscopic morphology of the peeling-off area of the water wall.

Figure 4 shows the SEM morphology of the peeling-off area of the water wall coating, in which a section of the residual coating is found. The left area indicated by the red arrow is the coating, and the right area is the base metal. Several micro cracks and oxide layers exist in the area where the coating and base material are combined.

Figure 4. SEM morphology of the peeling area of the water wall coating.
Note: Chinese characters (谱图 12-15) in figure mean points of energy spectrum 12-15.

3.2. Energy Spectrum Analysis
The energy spectrum analysis was carried out for both the sections of the normal area of the water wall coating and of the residual coating in the peeling-off area.

Figure 5 is the energy spectrum of the normal area of the water wall coating. According to table 1 (the energy spectrum analysis result of figure 1 in this paper) and table 2 (the energy spectrum analysis result of figure 2 in this paper), it is concluded that: Area 1 is the impurity area of the outer wall, in which exist a large amount of S element and combustion corrosion products; Area 2 is the hole-sealant area, the main component of which is sealant SiO₂, and there is a large amount of S element in this area; Area 3 is the supersonic flame spraying area of KM-99 wire, in which the main component is iron oxide compound with a few S element, indicating that S element has entered the coating through the sealing area. According to literature [6, 8], KM99 is an iron-based powder core wire (Fe 76.21wt%,...
Cr 16.33wt%), and Cr element level in area 3 is relatively low; Area 4 is the substrate 15CrMoG steel, main component Fe element.

Figure 5. Energy spectrum of the normal area of the water wall coating.

Table 1. Energy spectrum analysis result of figure 1 in this paper (wt%).

| Spectrum | Fe  | O   | S   | C   | Si  | Cr  |
|----------|-----|-----|-----|-----|-----|-----|
| Spectrum 1 | 67.7 | 25.3 | 1.0 | 4.4 | 0.9 | 1.2 |
| Spectrum 2 | 67.9 | 22.6 | 3.6 | 4.4 | /   | 1.5 |
| Spectrum 3 | 100 | /   | /   | /   | /   | /   |
| Spectrum 4 | 55.7 | 2.2 | 28.0 | 8.6 | 0.6 | /   |
| Spectrum 5 | 59.8 | 22.1 | 6.8 | 5.9 | 9.7 | /   |
| Spectrum 6 | /   | 54.4 | /   | /   | 45.5 | /   |
| Spectrum 7 | /   | 53.6 | /   | /   | 46.6 | /   |

Table 2. Energy spectrum analysis result of figure 2 in this paper (wt%).

| Spectrum | Fe  | O   | S   | C   | Si  | Zn  | K  | Na  |
|----------|-----|-----|-----|-----|-----|-----|----|-----|
| Spectrum 8 | 25.2 | 18.1 | 11.6 | 8.0 | 0.9 | 25.9 | /  | 3.2 |
| Spectrum 9 | 18.8 | 45.6 | /   | 11.0 | 17.3 | /   | 2.2 | /   |
| Spectrum 10 | 3.4  | 47.6 | /   | 18.9 | /   | /   | 3.1 | /   |
| Spectrum 11 | 8.6  | 22.4 | 11.6 | 18.1 | 18.7 | 18.7 | 1.9 | 1.9 |

Figure 6 is the energy spectrum diagram of the peeling-off area of the water wall coating. According to table 3 (the energy spectrum analysis result of figure 4 in this paper) it can be concluded that: Area1 is the impurity area, in which exist a large amount of S element and combustion corrosion products; Area 2 is the hole-sealant area, the main component of which is sealant SiO$_2$, and there is a large amount of S element in this area; Area 3 is the supersonic flame spraying area of KM-99 wire, in which the main component is iron oxide compound with a few Cr element, also a lot of micro-cracks inside, and a large amount of S element is found in the area combined with the sealant and the matrix. Area 4 is the substrate 15CrMoG steel, main component Fe element.
Figure 6. Energy spectrum of the peeling-off area of the water wall coating.

Table 3. Energy spectrum analysis result of figure 4 in this paper (wt%).

| Spectrum | Fe   | O    | S   | C   | Si  | Cr  | Mo |
|----------|------|------|-----|-----|-----|-----|----|
| 12       | 43.2 | 39.1 | 2.2 | /   | 0.5 | /   | 12.8|
| 13       | 57.9 | 36.1 | 6.0 | /   | /   | /   | /  |
| 14       | 84.2 | 5.5  | /   | 5.1 | 1.7 | 3.4 | /  |
| 15       | 53.3 | 37.4 | 1.5 | 7.8 | /   | /   | /  |

3.3. Analysis of Test Results

(1) Most part of the coating of the water wall tube has peeled off, and only a small area of the coating remained.

(2) There is only a small amount of Cr element the coating after KM-99 wire spraying.

(3) It was indicated that the S element has penetrated the sealing layer and corroded the substrate through the coating pores for the large amount of S element between the sealing agent coating and the small amount of S element found inside the coating.

(4) Microcracks were found in some areas of the residual coating, and a large amount of S element was found in the microcrack area. S element entered the interior of the coating through the pores of the coating, corroding the matrix structure, and reducing the bonding force between the coating and the matrix.

To sum up: The direct cause of the large-scale peel-off of the coating of the water wall pipe is that the element S penetrates the sealing layer and the anti-corrosion coating, then corrodes the substrate tightly bonded with the coating, thus the bond force between the coating and the substrate declines and microcracks appears; with gradient decrease of temperature from the coating to the inner wall of the tube, strong thermal stress appeared at the contact position of the coating and the substrate due to the influence of the structure of the water wall, the different thermal expansion coefficient and the thermal load. Microcracks under the influence of stress and corrosion continue to expand and extend, eventually cause the coating to peel off on a large scale and the tube fail.

4. Conclusion

It is inevitable that the pores and defects exist in the coating during the preparation process of thermal spray coating. The pores and defects in the coating will become the rapid mass transfer channel of the corrosive media, accelerating the corrosion of the coating and the substrate, thereby reducing service life of coating. It is effective to reduce the porosity of the coating and increase the service life of the coating by using sealant to seal the coating. It is low-cost, convenient-constructing to use a brushing sealant to seal the hole, but the effect could not be satisfied. The corrosive medium may reach the surface of the protected substrate through the perforation, causing chemical or electrochemical
corrosion between the coating and the substrate. The corrosion products accumulate at the interface, causing crack and peel-off the thermal spray coating, and ultimately the coating fail.

5. Suggestion
(1) Analyze the corrosive atmosphere of the water wall pipe, and choose different anti-high temperature corrosion spray materials according to different corrosive atmospheres. Targeted high-temperature anti-corrosion spray materials are the basis for the anti-corrosion capacity and durability of the coating.

(2) Control and track spraying materials, spraying process, coating performance, etc., to improve the service life of the coating.

(3) Improve the combustion environment of the boiler, reduce the reducing atmosphere of the flue gas at the inner wall of the water wall on the fire side of the boiler, reduce the swirling intensity of the external secondary air, thus to weaken the mixing intensity of the primary and secondary air outlet and increase the mixing intensity of the the tail primary air and secondary air, to enhance the oxygen concentration in the center of the furnace and increase the burnout rate in the center of the main combustion zone, thereby reducing the CO concentration in the middle part of the side wall and lowering the generation of H2S gas.

(4) Draw inferences about other cases from one instance. Carry out inspections in every shutdown, and strengthen the anti-wear and explosion-proof inspections in the areas such as both sides of the boiler, the area near the burners that are prone to high temperature corrosion.

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