Study on High-temperature Erosion Resistance of Precursor Ceramic Coatings

Songjie Yang, Jinqing Wang, Guangxin Wang*, Shiqi Tong, Zhimeng Wang, Mu’an Zhang, Zixiang Lin, Zhi Feng, Yunhao Xiong
Institute of Energy Engineering, China Jiliang University, Hangzhou, Zhejiang, 310018, China
*Corresponding author’s e-mail: 347547309@qq.com

Abstract. Given the high-temperature chlorine corrosion in the process of waste incinerators, polysilazane was used as the precursor, and glass powder and zirconia were added as fillers to prepare composite ceramic coating on TP347 substrate. In this paper, the effect of temperature on the formation of voids in the coating was studied by microscopic analysis. The high-temperature erosion wear resistance of the coating was also tested. The results show that the coating sintered at 500°C and 700°C has the best microstructure. To make the coating have higher hardness, the sintering temperature should be increased as much as possible at the allowable temperature of the substrate. The high-temperature erosion test shows that the erosion resistance of the coating is slightly lower than that of the substrate at room temperature and 400°C, but with the increase of temperature, the high-temperature erosion wear resistance is gradually enhanced, even exceeding the substrate, which is because the substrate is subjected to severe oxidation at high-temperatures, and its mechanical strength decreases with increasing temperature, while the coating is brittle at low temperatures, the erosion mechanism gradually becomes plastic as the temperature increases. The development of the shape erosion results in a much lower erosion wear at high-temperatures than the substrate.

1. Introduction
As the size of the city expands, so does the production of domestic waste. Incineration is one of the main methods of domestic garbage disposal. The method of incineration can reduce domestic waste by more than 85%, which plays a huge role in the treatment of municipal waste. Although the incineration method has certain advantages in the treatment of solid-liquid waste, a large number of elements such as K, Na, and Cl contained in the garbage form HCl, KCl, NaCl, and the like at a high-temperature. Therefore, compared with coal-fired boilers, waste incinerators face serious high-temperature chlorine corrosion problems during operation[1,2,3]. High-temperature chlorine corrosion will cause the wall thickness of the heated surface to be thinned, the strength will decrease, and eventually, the tube will burst, which will seriously endanger the safety during the operation of the boiler.

In order to mitigate the effects of corrosion, it is a common way to prepare a protective coating on a metal surface. At present, the main method is to prepare a corrosion-resistant metal coating on the heat exchange surface using thermal spraying or laser cladding. However, the actual situation proves that the coating prepared by thermal spraying is very easy to peel off, and the laser cladding is expensive. A large number of small and medium-sized enterprises have to reduce the corrosion of chlorine at the cost of reducing steam parameters, and some even use pouring to corrode. Treatment at severe locations severely jeopardizes heat transfer performance at local locations. Therefore, the development of a
coating with low cost, simple preparation and good corrosion resistance are of great significance for solving the high-temperature chlorine corrosion of boilers.

In the 1970s, with the development of silicone chemistry, Yajima et al. successfully prepared SiC ceramic fibres using organic polymer polycarbosilane \(^4\). The technique of using the thermal decomposition of the precursor to form the corresponding ceramic is the precursor ceramic technology (PDCs). Due to its simple preparation method, wide variety and low price, the precursor has been widely used in energy, environment, transportation and other industries\(^5, 6, 7\). Schütz et al. \(^8\) used polysilazane as a precursor and boron nitride as a filler to prepare a coating, and the resulting coating had a high porosity. A variety of different inert fillers have also been chosen, but none of them have a dense coating structure. Glass powder is a common filler. It can flow on the metal substrate after melting, wet the matrix and form the interface, and can enhance the adhesion of the coating itself and improve its compactness\(^9,10\). The author's team used polysilazane as a precursor, added glass powder and zirconia to prepare ceramic coating on the substrate, and studied its high-temperature chlorine corrosion resistance in previous work, which proved that it has excellent resistance, high-temperature HCl and KCl corrosion performance. The coating structure is dense, but there are some pores in the interior. This is because the polysilazane releases gas during the pyrolysis process, and the viscosity of the glass powder in the molten state decreases with increasing temperature, so the sintering temperature affects the coating. The discharge of gases in the layer, which in turn affects the coating structure. Also, due to the harsh internal environment of the boiler, the flow field characteristics are complex, especially the superheater is affected by the fly ash for a long time, so the coating must have strong erosion and wear resistance. At present, most of these studies are aimed at the mechanical properties of the precursor coating. For example, Xiao et al. \(^11\) studied the relationship between the Young's modulus of the coating, the hardness and the content of the Al expansion agent. Although the parameters such as hardness can reflect the wear resistance of the coating to a certain extent, the problem of erosion resistance of the precursor ceramic coating at high-temperature has rarely been reported in the literature.

In this paper, polysilazane was used as the precursor, glass frit and zirconia were added as fillers, and the coating was prepared on the substrate by the lift coating method. To study the effect of sintering temperature on the structure of coatings, the microstructure of coatings was observed by scanning electron microscopy (SEM) after sintering at 500°C, 600°C and 700°C, respectively. The high-temperature erosion resistance of the coating was also studied.

2. Experimental materials and methods

2.1. Slurry preparation

Adopting some kind of polyorganosiloxane as the precursor, a colorless transparent liquid, can soluble in ether and lipid solvent. It reacts violently with water. Next, polysilane dissolves in organic solvent-butyl acetate, glass flour and jargonia to add as filler. The softening temperature of glass flour is 500°C. Refer to table 1 for details. Then trace DCP to add as a radical initiator, stirring for 10 minutes with the electric agitator to form the slurry. Refer to table 2 for details.

| Table 1. Physical parameters of glass flour. |
|------------------------------------------|
| Average grain diameter/\(\mu m\) | Coefficient of thermal expansion/10\(^{-6}\).K\(^{-1}\) | Softening temperature/\(^\circ\)C | Density/g.\(\cdot\)cm\(^{-3}\) |
|------------------------------------------|
| 3.3 | 10 | 500 | 2.8 |

| Table 2. Chemical composition of coating. |
|------------------------------------------|
| Polysilane (Vol.%): Glass flour (Vol.%): ZrO\(_2\) (Vol.%): DCP (Vol.%): Dispersant (Vol.%): Butyl acetate (Vol.%): |
|----------------------------------------------------------------------------------|
| 14–54: 10–20: 10–20: 3: 3: 20–40: |
In order to filler particles have uniform distribution in the coating, grind the mixture of glass flour, ZrO$_2$, butyl acetate with the planetary grinder in advance, and add dispersant, making the dispersion of ultrasonic vibration.

2.1.1. Surface pre-treatment of the base material. This paper’s base material is waste incinerator superheater widely-used metal, TP 347; the size is 2×2×20mm. For better integration of base material’ surface and coating and preventing the influence of the experiment from base material’s surface behaviour, surface pre-treatment of the base material is necessary. Sandblasting the base material of composite ceramic coating sample which needs to preparation with quartz sand to that its surface derusting grade is Sa2.5-3. (average grain diameter of quartz sand is 420 μm, sandblasting pressure is 0.8 MPa), ensure that all base material have unified roughness. Later, ultrasound acetone cleaning base material, removal of oil pollution on surface and wash base material with alcohol, dry reserve.

2.2. Coating preparation
Smear ceramics slurry on the surface of the base material in the spraying method, after drying at room temperature sintering in Muffle Furnace. In the process of sintering, starting at room temperature, after heating to the final temperature at a heating rate of 3°C/min, keep warm for 2 hours, then drop to room temperature at a rate of 3°C/min. For the sake of researching sintering temperature making a difference to the property of coating, set final temperature at 500°C, 600°C, 700°C.

2.3. Anti-wear performance study
The high-temperature erosion wear test is to study the erosion and wear characteristics and mechanism of the coating at high-temperature. The test is carried out on a self-made high-temperature erosion test bench. The test bench is built according to the standard ASTM G76-07. The compressed air is discharged from the air compressor and then removed by the freeze dryer. After being mixed with the abrasive in the storage tank, it is sprayed through the nozzle, and the sample is fixed at the nozzle. The erosion temperature is adjusted by an electric resistance furnace, the flow rate is adjusted by a pressure reducing valve, and the abrasive flow rate is adjusted by a ball valve.

The test temperature is room temperature, 400°C, 450°C, 500°C, 550°C, 600°C, the compressed air flow rate is 16 m/s, and the abrasive is made of quartz sand with an average particle size of 50μm. The flow rate is 20 g/min. The test procedure is as follows:

1) Weigh the sample of the initial mass and record it as $A_0$.
2) Fix the sample on the fixture, weigh 20 g of quartz sand into the storage tank, set the heating program to start heating the sample, and open the gas valve.
3) After the temperature is stabilized, the feed valve is opened and the erosion test is started.
4) After the erosion is completed, the sample is taken out, washed with absolute ethanol, dried and weighed, and recorded as $A_i$ (i is the number of tests).
5) Cycle steps 2 to 4 for a total of 10 times, and if it is found to be ground to the substrate, the test is terminated.
6) Microscopic analysis of the morphology of the coating after high-temperature erosion using a scanning electron microscope.

In this paper, the weight loss method is used to characterize the weight loss characteristics of the sample, and the weight per unit area of the sample is defined as $\Delta A_i$:

$$\Delta A_i = \frac{A_i - A_0}{4}$$

In the above formula, $A_i$ is the mass weighed after taking the sample for the i-th time, and $A$ is the surface area of the sample.
3. Results and discussion

3.1. The influence of sintering temperature on the coating structure

We sinter polysilazane/the glass powder/zirconia composite coating under 500°C, 600°C, and 500°C respectively, and observe the microstructure of the section, the results are shown in figure 2. The results show that the thickness of the coatings sintered at three temperatures is 50-60μm, which indicates that the influence of sintering temperature on the thickness of the coatings is small. When the sintering temperature is 600°C, the sizes of holes in coating are about 20 to 30 microns, and when the temperature is between 500 to 700°C, the internal coating significantly shrink hole size, the sizes of holes are most under 10 microns, the size of the biggest hole is only about a third of the total thickness of coating. This is because when the sintering temperature is 500°C, the structure of the coating is relatively loose, and the internal holes showed irregular shape. At this time, the glass powder is not fully molten, so the exhaled gas can discharge through the interstice of the glass powder. And when the sintering temperature is 700°C, the glass powder has been completely melted, and the viscosity is lower than 600°C, so the exhaled gas separates out easily through the coating. By figure 2 (c), the size of the internal holes is slashed at this time, and the structure is more compact.

To sum up, the sintering temperature has great influence on the hole size in the coating. When the sintering temperature is above the softening temperature of the glass powder about 100°C, porosity of coating and the hole size are maximal. And when the sintering temperature is lower than the softening temperature of the glass powder or higher than softening temperature above 200°C, the coating porosity and the hole size can be reduced significantly. However, the hardness of coating increases with the increase of sintering temperature. Therefore, the sintering temperature should be increased as far as possible under the allowable temperature of the substrate.
Sintered under 500 °C  
(a) Sintered under 500 °C  
(b) Sintered under 600 °C  
(c) Sintered under 700 °C

Figure 2. Section morphology of coating after sintering at different temperatures.

3.2. High-temperature erosion wear

To study the erosion-wear resistance of coating with the change of temperature, high-temperature erosion wear tests are carried out respectively at room temperature, 400°C, 450°C, 500°C, 550°C and 600°C, and the chosen coatings are sintered under 700°C.

Figure 3 shows the curve of TP347’s weight loss per unit area over time at different temperatures. Figure 4 shows the coating of weight loss per unit area over time at different temperatures of the coating.

The slope of the fitting equation is the erosion wear rate of the basic material, which can be used to characterize the erosion wear resistance of the material. According to the erosion wear rate of the basic material at different temperatures, the erosion wear resistance of TP347 decreases with the increase of temperature. This is because the increase of temperature will decrease the yield strength, hardness and other mechanical properties of TP347, thus resulting in a decline in its ability to resist erosion wear. According to Figure 3, the erosion wear rate of basic material at room temperature and 400°C have no significant difference. However, there is an obvious rise when erosion temperature is 450°C. The specific performance is the rate change from 0.0005 mg·cm⁻²·s⁻¹ when it’s 400°C to 0.0297 mg·cm⁻²·s⁻¹ when it’s 450°C, rising by 0.0292 mg·cm⁻²·s⁻¹. This is because when the temperature is 400°C, the surface of basic material is oxidized, then Fe₂O₃, Cr₂O₃ and any other protective films are generated. These protective films have a higher hardness than the matrix in the same temperature, leading to the erosion wear rate of basic material at room temperature similar to 400°C. But when the temperature is higher than 400°C, due to the different thermal expansion coefficient, the oxide film is easy to crack and peel off, so that the matrix is exposed to the erosion environment, resulting in a sharp increase in the erosion wear rate.

In the process of boiler operation, the temperature of the superheater tube wall is usually above 400°C. From the above, metal in this position is not only affected by high-temperature erosion, but also goes through the cycle of high-temperature oxidation-oxidation film peeling - matrix thinning, which speeds up the thinning speed of superheater tube wall.
Figure 5 shows the change curve of erosion wear loss rate of coating and substrate with temperature, by figure available, When the temperature is 400°C, the coating of erosion wear rate is higher than that of the coating at room temperature erosion wear rate, but with the increase of temperature, coating of erosion wear rate is declining, the lowest was achieved when the temperature is 550°C. Contrast erosion wear rate change characteristics of coating and base material, when under room temperature and 400°C erosion wear rate of coating is higher than the base material, but the gap is not big, explain coating under the two temperature erosion wear resistance is slightly inferior to the base material. But when the temperature higher than 400°C, the base material of erosion wear rate rising sharply because of the falling on the mechanical properties of the base material and oxidation film of spalling failure. However, the coatings with temperature erosion wear rate are falling, resulting in 400°C after the high-temperature erosion resistance of the coating was much higher than that of the base material, and as the temperature rises, the gap is bigger and bigger. This indicates that the high-temperature erosion wear at the superheater is very severe in the actual operation process. After the application of the coating, not only the erosion wear resistance of the heat exchange surface is improved, but also the substrate is effectively prevented from being oxidized, which can greatly delay the tube wall thinning rate of the superheater.

Figure 5. Erosion loss rate of coating and substrate at different temperatures.

3.3. The surface morphology of the coating at different erosion temperatures. Using scanning electron microscope (SEM) to room temperature and 450°C, 550°C and 600°C under the erosion surface morphology of the coating after observation to investigate the resistance of the coating at high-temperature erosion wear mechanism, the results are shown in figure 6.

(a) Room Temperature, 500×  
(b) Room Temperature, 5000 ×
By the figure, the coating surface morphology after erosion wear, great changes have taken place in the smooth surface of the original, was full of large and small holes. These holes within a few microns to 20 microns in diameter, is formed in the process of sintering, because of erosion wear, the coating surface had been destructed, making internal holes exposed. By comparing coating surface morphology after erosion wear at various temperatures, it can be found that at room temperature and 450°C the surface morphology of coating is consistent and the distribution of the exposed stomach is uniform.

Figure 6 (b) and figure 6 (d) is the micro enlarge figure of coating, under room temperature and 450°C after the erosion, both can be found that surface has obvious residual traces of peeling off. Also, local location can be found the phenomenon of crack and collapse, it is caused by the interlace of transverse and longitudinal crack in the erosion process, it will make the coating lose the bottom of the support material in the case of surface integrity, leading to the collapse and peeling of the coating. This mechanism is typical brittle material erosion wear, so the coating at room temperature to 450°C, its erosion wear mechanism is brittle erosion.

Figure 6 (e) and figure 6 (g) is the surface morphology of coating under 550°C and 600°C after erosion. According to the figure, on the surface of the coating, although a large number of stomates are exposed under the two temperature, their distribution is not uniform but is the irregular regional distribution, and stomatal brittle erosion effect is less obvious than in low temperature. Besides stomatal area, the rest erosion position still maintains good surface condition, did not appear the phenomenon such as peeling, broken. This is the direct cause of erosion wear low rate under 550°C and 600°C. This regional
distribution is more obvious with the increase of temperature, because the increase of temperature leads to the softening of glass powder, and the higher the temperature is, the more viscous the glass powder is. At this point, the brittle erosion gradually develops to the shape erosion, the abrasive hitting on the coating does not cause the coating material to break up and flake off like the brittle erosion, but only causes the plastic deformation of the coating material.

These plastic deformations occurred in the soft position of the coating and could recover under the influence of high-temperature, resulting in the regional distribution of the exposed pores after the coating was eroded by high-temperature.

4. Conclusion
In this paper, polysiloxane was used as a precursor, glass powder and zirconia were added as filler to prepare the coating on TP347 substrate, and the influence of temperature on the formation of pores in the coating was studied. The main conclusions are as follows.

(1) Temperature has a significant impact on the generation of holes in the coating sintering process. To reduce the size of holes and make the coating have a higher hardness, the sintering temperature can be increased as far as possible under the allowable temperature of the substrate.

(2) High-temperature erosion wear test showed that the erosion wear resistance of the coating at room temperature and 400°C, less base material, but with the increase of temperature, high-temperature erosion wear resistance of the coating gradually strengthened, even more than the base material. This is because the substrate is subjected to severe oxidation at high-temperature, and its mechanical strength decreases with the increase of temperature, while the coating is brittle erosion at low temperature. With the increase of temperature, the erosion mechanism gradually develops to plastic erosion, resulting in its erosion wear at high-temperature is much lower than that of the substrate.

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