Slagging resistance mechanism of precursor ceramic coating for solid fuel-fired boilers

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Abstract. Slag formation on the heating surface in solid fuel-fired boilers is a common problem. In this paper, with polysilazane used as the precursor, three different ceramic coatings were prepared by adding hexagonal boron nitride (h-BN), ZrO\textsubscript{2}, and Al\textsubscript{2}O\textsubscript{3} inert fillers. The coatings were applied to a TP347 substrate by the Czochralski method. The spreading and solidification experiments of the molten ash were performed and matched with numerical simulation. The results show that compared with the steel sheet, the molten ash has a large contact angle on the coating, a small spreading coefficient and the same spreading time, indicating that the coating has the slagging resistance property. The coating with the addition of h-BN has better slagging resistance properties than the other two coatings. The numerical simulation results are consistent with the experimental results.

1. Introduction

Boiler slagging is common in solid fuel-fired boilers such as coal-fired boilers and waste incinerators. The slagging on the heating surface of the boiler will reduce the thermal efficiency of the boiler and increase the emission of nitrogen oxides. More seriously, some accidents such as superheater bursting, furnace stalling, and water wall damage may occur, which will threaten the safe and economic operation of the boiler\textsuperscript{[1][2]}. To resist the slagging problem, many measures have been proposed, including a reasonable design of the combustion system\textsuperscript{[3]}, installing soot blower\textsuperscript{[4]}, blending weakly slag coal\textsuperscript{[5]}, adding additives\textsuperscript{[6]}, spraying protective coating and so on. While, there are few studies on protective coatings compared to general measures.

Naganuma et al.\textsuperscript{[7][8]} prepared different ceramic materials on the heating surfaces by thermal spraying technology, and found that the bonding strengths of the molten ash to different materials were different. Typically, the nickel alloy coating could effectively slow the slagging. Chen et al.\textsuperscript{[9]} also found that it can reduce the adhesion strength of molten ash by thermal spraying a nickel-containing coating. Formanek et al.\textsuperscript{[10]} sprayed a ceramic coating containing aluminum oxide and chromium oxide on the water wall to reduce the contamination and corrosion of the heated surface. However, thermal spraying technology has the disadvantages of high cost, low utilization rate of spraying materials and it is difficult to operate. These limit its promotion and development\textsuperscript{[10]}. Shan et al.\textsuperscript{[11]} synthesized a ceramic coating with good impact resistance and oxidation resistance on the chrome-manganese alloy substrate by slurry method. Wang et al.\textsuperscript{[12][13][14]} prepared a composite ceramic coating for the high-sodium coal, high-
sulfur coal, high-alkali coal and other easily-slagging coal by slurry method. In the laboratory, it was found that the coating with h-BN added had good adsorption resistance, shock resistance and stain resistance. They have been applied to a Zhundong coal boiler and achieved good results. However, this composite coating produces some cracks that shorten the life.

Precursor ceramic coating technology can alleviate the above problems. The technology has advantages of low energy consumption and simple spraying. With the features of organic polymer and ceramic materials, the coating is not easy to crack, owning high hardness, good wear resistance and hydrophobicity. However, during the pyrolysis of the precursor, the volume shrinkage due to gas escaping, which leads to defects, cracks and even delamination of the coating. For single precursor coating, the critical thickness is too small and not conducive to the use of the coating in harsh environments. Greil et al.\cite{15} first proposed the addition of active fillers in the precursors to alleviate the problems caused by the volume shrinkage of the precursors, and established a physical model for the volumetric shrinkage during the cracking process. Schütz et al.\cite{16} used glass frit as a filler to densify the coating for the increase of coating thickness and adhesion. The addition of a low surface energy material to the precursor can improve the slag resistance of the coating. Different from other coating measures, the precursor ceramic coating technology first uses a chemical method to synthesize a precursor cross-linked polymer, which is then pyrolyzed to form a ceramic coating. The coating can be sprayed on the heated surface by a general spraying method.

In this paper, three kinds of ceramic coatings were prepared by respectively adding the inert fillers hexagonal boron nitride (h-BN), ZrO\(_2\) and Al\(_2\)O\(_3\) with the precursor method. The three types of coatings were subjected to a melt diffusion and solidification test using a slagging test apparatus. The slag resistance of the coatings was evaluated and compared by studying the contact angle, diffusion coefficient and temperature of the droplet and the coating, combined with numerical simulation.

### 2. Experiment and simulation

#### 1. Preparation of coating

**1.1 Preparation of slurry.** First, the slurry was prepared with the precursor method. The organopolysilazane was used as the precursor, butyl acetate was used as the solvent, dicumyl peroxide was used as the free radical initiator. Three inert fillers h-BN, ZrO\(_2\) and Al\(_2\)O\(_3\) were added separately. The components were uniformly mixed with a stirrer for 30 minutes to obtain three composite ceramic slurries. The proportions of the three slurries components are shown in Table 1.

| Polysilazane (Vol.\%) | h-BN/ ZrO\(_2\)/ Al\(_2\)O\(_3\) (Vol.\%) | Butyl Acetate (Vol.\%) | Dicumyl peroxide (Vol.\%) |
|-----------------------|------------------------------------------|-------------------------|---------------------------|
| 40                    | 30                                       | 27                      | 3                         |

**1.1.2 Preparation of coating samples.** The coated steel piece was made of TP347 steel and cut into squares of 20 mm × 20 mm × 1 mm. In order to facilitate the embedding of the thermocouple, a 1 mm hole is made in the center, and a groove of 0.5 mm in depth and 1 mm in diameter is dug at the right side of the back, as shown in Figure 1.

![Figure 1. Schematic diagram of the opening of the sample piece.](image)

To begin with, it was sandblasted with quartz sand having an average particle diameter of 40 μm for
coating adhesion and sintering. After that, the surface oil was cleaned with ultrasonic acetone. Finally, it was washed with alcohol and dried.

Thereafter, the slurry was applied to the steel sheet by the Czochralski method, and the critical thickness of the coating was about 20 μm. In order to prevent bubbles or cracks in the coating caused by direct heating, the steel sheet covered with the coating was first placed in a dry oven and heated from room temperature to 85°C at a heating rate of 3°C/min, dried for 1 h. After drying, it was placed in a muffle furnace and heated to 600°C at a heating rate of 3°C/min, kept for 2 h. Finally, it is taken out after cooling along with the furnace.

1.1.3 Comparative steel sheet specimen. During the actual slagging process, the object of adhesion of the molten ash is mainly derived from the oxide film layer of the steel. Therefore, for comparison, the tp347 steel sheet was subjected to the same washing and drying step, placed in a muffle furnace for high-temperature oxidation, with an oxidation temperature of 500 °C and an oxidation time of 24 hours, to form a dense oxide film on the surface.

1.2 Molten ash spreading and solidification experiment
In the slagging testing device (Figure 2), the simulated ash was poured into a corundum tube. The simulated ash composition was shown in Table 2. First, the simulated ash was melted into liquid in a high-temperature frit furnace (1300°C), and the corundum tube was quickly lowered to 3 cm from the sample piece. In a high temperature electric furnace (700 °C), the droplets were dropped into the center of the sample piece on the cooling and temperature measuring device (Figure 3) by means of a syringe at the top of the pressurized corundum tube. In order to avoid too high content of the oxygen, N₂ is introduced into the furnace to provide a reducing atmosphere. The high-speed camera shoots through the high-temperature glass observation hole provided in the lower part of the high-temperature electric furnace. The wettability of the coating was analyzed by measuring the contact angle. The pressure of the compressed air (0.2 MPa) introduced into the cooling device was controlled by a pressure regulating valve to maintain the upper sample piece of the cooling device at 500°C. When the droplet drops into the center of the sample, the thermocouple in the temperature measurement hole can measure the temperature of the droplet, and the temperature of the droplet can be transmitted by the data acquisition card (DAQ) to the computer for the temperature change recording.

![Diagram of slagging testing device](image1)

![Diagram of cooling and temperature measuring device](image2)

| Na₂O/% | BaO/% | SiO₂%/ | CrO₃%/ | Al₂O₃%/ | Softening Temperature /°C |
|-------|-------|--------|--------|---------|--------------------------|
| 5     | 40    | 30     | 15     | 10      | 680                      |

Figure 2. Diagram of slagging testing device.
Figure 3. Diagram of cooling and temperature measuring device.
In order to avoid the influence of the placement of the thermocouple on the measuring point and the temperature in the vicinity thereof, the groove and the temperature measuring hole are buried. In order to measure the temperature of the droplets passed through the through holes in the center of the sample piece, two thermocouples with ceramic sleeves were placed in the grooves of the cooling device. The thermocouple probe that measures the temperature of the sample piece is placed in the groove on the right side of the sample piece to measure the temperature of the sample piece.

The contact angle is the angle between the tangent of the gas-liquid interface and the boundary between the liquid and the solid-liquid, expressed by $\theta$. The JC2000 was used to measure the contact angle of the spreading coagulation process recorded by the high-speed camera. During the measurement, multiple steel plate samples and three coating samples were taken and averaged to obtain the final contact angle data. Since the solid surface has a roughness $r$, the measurement results need to be corrected according to the Wenzel equation\textsuperscript{[17]} $\theta_w$ in the formula is the true contact angle.

$$\cos \theta_w = r \cos \theta \tag{1}$$

The dynamic diameter of the contact surface of the droplet to the sample piece is $d$. The ratio of the dynamic diameter $d$ and the equivalent diameter $D$ of the droplet is the spreading coefficient $\beta$, which can be used to characterize the wettability of the liquid to the solid.

$$\beta = \frac{d}{D} \tag{2}$$

During the measurement, the spreading coefficients of the steel sheet and the three coated samples were each taken from a plurality of data and averaged to obtain the final spreading coefficient.

1.3 Numerical simulation of molten ash

From the above experiment, it was found that the h-BN coating has the best resistance to the slagging effect. However, the information such as the temperature distribution inside the droplet, the spreading and solidification process of the droplet, could not be obtained. Thus, the numerical simulation is further carried out. By analyzing the shape and temperature field changes of the droplets, and measuring the parameters such as contact angle and spreading coefficient, the numerical simulation is well instructive compared with the experimental results.

The multi-phase flow VOF method is used to track the liquid-gas interface, and the DO model is used to solve the radiation heat transfer problem during the droplet movement. The solidification/melting model was combined with the VOF model to solve the solidification problem after the droplets contacted the substrate. The physical property parameters are shown in Table 3.

| Materials                  | Simulation Ash | Air       | Sample Piece         |
|----------------------------|----------------|-----------|----------------------|
| Density ($\text{kg/m}^3$)  | 2500           | 0.362     | 7850                 |
| Specific Heat (J/kg·K)     | 700            | 1135      | 460                  |
| Thermal Conductivity (W/m·K)| 1.1            | 0.1671    | 61(steel sheet)      |
|                            |                |           | 59(h-BN)             |
| Viscosity (Pa·s)           | 0.25           | 4.15e-5   | /                    |
| Solids Temperature (K)     | 953.15         | 0         | /                    |
| Liquidus Temperature (K)   | 953.15         | 0         | /                    |
| Surface Tension (N/m)      | 0.56           | /         | /                    |
| Initial Contact Angle (°)  | /              | /         | 91.574(sheet steel)  |
|                            |                |           | 126.142(h-BN)        |
The initial contact angle of the two sample pieces are the final contact angles which was measured by the melt ash spreading and solidification experiment.

2. Results and discussion

2.1 Morphology analysis

The simulated droplet diameter was 7 mm, the collision speed was 0.75 m/s, and the initial position was the point contacted with the sample piece. The simulated picture of the morphological change of the molten ash on the steel sheet and the h-BN coating were spliced with the experimental photograph, as shown in Figure 4. It can be seen that the simulation results are almost identical to the experimental results. After the droplets on the steel sheet begin to deposit, they gradually spread on the substrate, and the radius increases continuously. However, due to the high temperature of the droplets and the low temperature of the ambient air and the substrate, the heat exchange between the three is very intense, resulting in short spreading process time. The leading edge of the intermediate droplet solidifies in a short time, and the droplet spread is insufficient. When the droplets are deposited on the substrate, the air just below the droplets is drawn into the droplets because it is too late to be discharged. The deposition process of the droplet on the h-BN coating is short, the contact area of the droplet with the substrate is small, and after the speed is reduced, it is almost no longer spread.

![Figure 4. Diagram of morphological comparison. In the experiment and simulation, the morphological changes of the droplets on the steel sheet and the h-BN coating were compared.](image)

2.2 Contact angle

The change in the contact angle of the molten ash on each sample piece with time in the experiment and simulation is shown in Figure 5.

According to the change of the contact angle of the three coatings and the steel sheet, the contact angle of the molten ash on the steel sheet gradually decreases with the increase of time. On the coating, the contact angle first decreases and then increases with time. Mainly because the molten ash spreads slowly under the action of the coating, and the contact angle gradually decreases. When the contact line stops spreading, the upper part of the molten ash continues to deposit downward under the action of inertial force and gravity, so the contact angle gradually increases. The contact angle of the final molten ash on the three coatings is larger than that of the steel sheet. Among the three coatings, the contact angle of the molten ash in the h-BN coating is the largest, which is 34.7° larger than that of the steel sheet. It indicates that the coating weakens the wettability of the molten ash, and the addition of the h-BN filler to the precursor is more effective.
In the numerical simulation, the contact angle of the droplet on the steel sheet gradually decreases with time, and the simulated value of the contact angle is larger than the experimental value. After the droplet solidification stops spreading, the numerically calculated contact angle is $93^\circ$, and the final angle is $91.3^\circ$ through experimental measurement. The simulated value of the contact angle of the droplet on the h-BN coating is generally smaller than the experimental value. After the droplet deposition is completed, the experimental value is $1^\circ$ smaller than the simulated value. The simulation results agree well with the experimental results.

![Figure 5. Curves of contact angle versus time.](image1)
![Figure 6. Curves of spreading coefficients versus time.](image2)

### 2.3 Spreading coefficient

Figure 6 shows the curves of the spreading coefficients of the molten ash on steel sheets and coatings with time in experiments and simulations. It can be seen that the spreading coefficient of the molten ash increases with time. Due to the higher initial molten ash temperature, the viscosity is smaller and the spreading is faster. As time increases, the temperature at the bottom of the molten ash and the spreading speed decrease gradually. The molten ash reaches a spread balance at 9 ms and no longer spreads with a spreading coefficient of 0.96.

The spreading coefficient of the molten ash on the h-BN coating reaches a maximum value of 0.77 at 6 ms. The molten ash on the ZrO$_2$ coating no longer spreads at 6 ms, and the spreading coefficient is 0.8. On the Al$_2$O$_3$ coating, the spreading coefficient reaches a maximum value of 0.81 at 7 ms.

As can be seen from the figure, when the molten ash no longer spreads, all the spreading coefficients on the coating are smaller than those on the steel sheet. The molten ash needs a shorter time to reach the spread balance on the coating. The results indicate that the coating weakens the wettability of the molten ash. After the spreading stops, the spreading coefficient of the molten ash on the h-BN coating is the smallest, which is 0.19 smaller than that of the steel sheet. It shows that the wettability of molten ash on h-BN coating is the worst. This results in a smaller contact area of the sample piece, which makes the adhesion of the molten ash difficult and finally achieves the effect of slagging resistance.

The simulated value of the spreading coefficient of the droplet on the steel sheet is slightly smaller than the experimental value. After spreading, the simulated value is 1.84% smaller than the experimental value. The experimental and simulated spreading coefficients of the droplet on the h-BN coating differ by 1.82%, which is in good agreement.

### 2.4 Temperature change

During the simulation, the temperature monitoring point is set at the same position as the experiment, in the center of the droplet. This shows the temperature change of the droplet on the steel sheet and the h-BN coating. The comparison between the experimental and simulation results is shown in Figure 7. The temperature changes are similar. When the molten ash is dropped onto the steel sheet and the coating,
the temperature of the sample piece is about 860°C. From the analysis of the spreading coefficient, it can be seen that the spreading of molten ash stops at 7 ms, the temperature of the molten ash measured at 840°C is higher than the solidification temperature, indicating that the front edge of the molten ash has been solidified. With the passage of time, the molten ash gradually cools from the bottom, the molten ash temperature reaches 680°C at 1 s, which is the solidification temperature, and the molten ash is gradually solidified. Therefore, most of the solidification during the spreading process occurs after the solid-liquid-vapor contact line stops, and the local solidification at the molten ash contact line controls the stop point of the contact line, which plays a central role in determining the final shape of the deposited droplet.

During the simulation, the temperature of the droplets rapidly decreases when spreading on the substrate. Compared with the experimental data, the temperature decreases rapidly. It is stable at 500°C after 8 s. This is because thermocouple temperature measurement requires a certain response time during the experiment.

Figure 7. Curves of temperature versus time of steel sheet and h-BN coating in the experiments and simulations.

2.5 Slagging resistance mechanism of precursor coating
The slagging resistance mechanism is shown in Figure 8. The melted or partially melted particles carried by the flue gas are cooled and solidified on the heating surface, resulting in slagging of the boiler. When the molten ash diffuses and impacts on the precursor ceramic coating, the contact angle of the droplets is greater than 90° due to the wettability of the coating, resulting in residual air between the droplets dispersed on the coating. The area between the molten ash and the heating surface becomes smaller. When the molten ash accumulates into a slag, the adhesion between the molten ash and the heating surface is insufficient, causing it to fall off. Then the slag prevention effect is achieved.
3. Conclusions

(1) The molten ash has poor wettability on the surface of the coating, and the h-BN coating is the worst. The contact angle of molten ash on the coating is more than 90°, and the spreading coefficient is much smaller than 0.96 of the steel sheet. The contact angle of the h-BN coating surface is 34.7°. The spreading coefficient is reduced by 0.19 compared with the surface of the steel sheet. The spreading coefficients of the ZrO₂ coating and the Al₂O₃ coating are also reduced by 0.16 and 0.15, respectively. The results show that adding h-BN to the coating has better slag resistance characteristics than the other two fillers.

(2) The temperature changes of the droplets between the steel sheet and the coating are very similar. The solidification process of the droplets is independent of the sample. The difference between the simulated and experimental values of the contact angle is not more than 2°, and the difference between the simulated and experimental values of the diffusion coefficient is not more than 1.84%, which is in good agreement. The simulation results show that the wettability of the droplets on the coating is poor, which is consistent with the experimental results.

(3) Slagging resistance mechanism of the precursor coating is to reduce the wettability of the heating surface, so that it cannot be completely spread and reduce the contact surface. Eventually it will fall off due to the insufficient adhesion.

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