Preparation and Research of Nano Water-Based Ultra-Thin Fire Retardant Coatings for Steel Structure

Shijie Gao¹,², * Jianyong Liu¹,², Xin Wu¹,² and Yulong Wu¹,²

¹Guangzhou Building Material Institute Limited Company, Guangzhou
²Guangdong Province Enterprise Key Laboratory of Materials and Elements Fire Testing Technology, Guangzhou

*Corresponding author e-mail: gaoshijie2012@126.com

Abstract. The effects of nanometre materials on fire retardant coatings for steel structure were prepared and studied. The results showed that there were many bubbles in the Nano coating, and the carbon layer was more complete and compact. At the same time, the heat release rate, total heat release and smoke production rate of Nano coatings are all lower than traditional coatings. According to XPS energy spectrum analysis of the Nano coating, the content of O element in the black region is lower, and the content of P element is higher than that in the white region, indicating that the combustion in the black region is not complete and the flame retardant effect is better.

1. Introduction

Steel structure materials are widely used in construction engineering. Compared with traditional materials, steel structure materials have stronger mechanical properties, smaller space structure, higher use efficiency, recyclable, and more economical and environmentally friendly [1]. At present, many tall and complex buildings in the world use steel to complete their main structure [2]. However, due to the very large thermal conductivity of steel, in case of high temperature fire, the mechanical properties of steel structure materials will rapidly decrease, or even lose their supporting capacity, leading to serious disasters [3]. For example, in the event of September 11, 2001, a fire broke out in the world trade building in New York, USA, which was a steel structure. As a result of the high temperature, the elastic limit and yield strength of the steel decreased rapidly, and the ultimate bearing capacity of the steel was lost, leading to the disaster of the century [4].

According to statistics, general steel will lose its mechanical support when the temperature reaches 540°C. When a building fire occurs, the temperature will quickly rise to more than 700°C [5]. Therefore, there are serious fire safety risks in the use of steel structure materials, which is of great significance to the research on fire prevention of steel structure materials.

The water-based fire retardant coating is a hot spot in the current research, which is green and non-toxic [6]. In this paper, a new type of Nano water-based fire retardant coating is developed, which improves the comprehensive performance of water-based ultra-thin steel structure fire retardant coating by using the characteristics of small specific surface area and high activity of Nano particles, and compares with the traditional steel structure fire retardant coating [7].
2. Preparation of fire retardant coating and test

2.1. Traditional fire retardant coating
The main raw materials of traditional fire retardant coatings are titanium dioxide, ammonium polyphosphate, melamine, pentaerythritol, water, surface agent, defamer, AMP-95, emulsion, thickener, Propylene Glycol, bactericide, film builder, cellulose ether, etc. Each raw material is grinded and filtered by adding a certain proportion with some sequence to the agitator, and finally discharged to obtain the required traditional water-based fire retardant coating.

2.2. Nano fire retardant coating
Nano fire retardant coating is added Nano-sized acicular calcium silicate, and through a certain time of mixing and grinding, which based on the traditional fire retardant coating.

2.3. Sample preparation
Prepare 6 stainless steel plates with the size of 100mm * 100mm * 1mm, then polish, clean and dry them. Brush the prepared two fire retardant coatings on the stainless steel plate evenly to achieve the set thickness and ensure that the coating surface is flat and even without obvious convex and concave.

Put the prepared sample into the regulating chamber with the temperature of (23 ± 2)°C, humidity of (50 ± 5)%, and the regulating time of at least 72 hours, until the mass is balanced, and there is no obvious sticking or collapse when the surface is touched.

2.4. Test device
The test device is a cone calorimeter manufactured by British FTT Company. The test principle is the oxygen consumption principle, that is, the heat released per unit mass of oxygen consumed by material combustion is (13.1 ± 5%) MJ/kg. The main test parameters are the heat release rate, total heat release, mass loss rate, smoke production rate, effective combustion heat, etc. The test device is shown as below:

![Cone calorimeter](image)

**Figure 1.** Cone calorimeter.

2.5. Test condition
Laboratory environment: Temperature is 15°C ~ 30°C, Relative humidity is 20% ~ 80%, and there is no obvious airflow disturbance.

Test conditions: the temperature is 700°C, and the test can be started after it is stable at least 10 minutes; The exhaust flow is (0.024 ± 0.002) m³/s; The data collection cycle is 5s, and the test time is 30min.
During the test, the sample is wrapped with a single-layer aluminum foil with a thickness of 0.025mm - 0.04mm, so that the glossy side faces the sample, then put sample into the holder, and the redundant aluminum foil is cut off to expose the test area. Place the sample horizontally, and the distance between the surface of the sample and the bottom of the conical heater is 50mm.

3. Test result and analysis

3.1. The appearance of samples before and after the test

The photos of samples before and after the test of traditional coating and nano coating are shown in the following figure:

![Before the test](image1)
(1) Traditional coating  (2) Nano coating

![After the test](image2)
(3) Traditional coating  (4) Nano coating

**Figure 2.** Photos of samples before and after the test.

It can be seen from the photos that before the test: the surface of traditional coating and Nano coating basically meets the requirements of smoothness and no obvious defects. After the test: the number of bubbles of the traditional coating in which some of them fall off is less than the Nano coating, and the volume is larger. The number of bubbles of the Nano coating is much more, the volume is small, and the arrangement is close and uniform, without falling off, and the appearance is darker than that of the traditional coating. The results show that the expansion of the traditional coating is better than that of the Nano coating, but the strength is lower than that of the Nano coating. At the same time, due to the incomplete combustion of the Nano coating, the products are mostly black materials which are not completely oxidized, so the flame retardant effect of the Nano coating is better.
3.2. Test result
In figure 3, figure 4 and figure 5, sample 1 is traditional coating and sample 2 is Nano coating. It can be seen from the figures that the ignition time of traditional coating is earlier, and the peak heat release rate, total heat release and smoke production rate are all higher than Nano coating. This indicates that the Nano coating can form a carbon layer with better thermal insulation performance during combustion, which can delay the ignition time of the coating, and reduce the heat release rate, total heat release and smoke production.

**Figure 3.** Heat release rate curve.

**Figure 4.** Total heat release curve.
3.3. Scanning electron microscope analyses

The fire-retardant effect of the fire-retardant coating is closely related to the structure of the carbon layer formed after the combustion, so it is necessary to further analyze the sample after the test by using the scanning electron microscope, which is shown in Figure 6 and Figure 7.

It can be seen from the figures that the carbon layer structure of the traditional coating is not dense enough, and there are many holes in the carbon layer, and honeycomb structure can be seen clearly inside the holes; The electron micrograph of the Nano flame retardant sample shows that the sample surface after combustion also has obvious carbon layer structure, and the carbon layer structure is more complete, dense and stronger than that of the traditional flame retardant sample, The flame-retardant performance of the samples should be better than that of the traditional samples.

One of the reasons for this difference may be that the manufacturing process of Nano coating and traditional coating is different. The traditional coating is the classic flame retardant system of ammonium polyphosphate, melamine and pentaerythritol plus other color fillers and additives, while the Nano coating is pre-dispersed with Nano-level melamine and ammonium polyphosphate, so that the surface of ammonium polyphosphate is evenly coated with a layer of Nano-size melamine. Under the condition of flame combustion, every reaction point of ammonium polyphosphate has the synergistic reaction of melamine with the oxygen. Therefore, the carbon layer after the combustion of the Nano coating is dense and uniform. The carbon layer seals the combustible materials inside the coating, making it difficult for the combustible gas inside to escape, and the external heat and oxygen cannot reach the inside of the coating, so as to improve the flame retardant effect.

Figure 5. Total smoke production curve.
Figure 6. Conventional coating electron microscopes.

Figure 7. Electron microscope of Nano coating.
3.4. Energy spectrum analysis

Figure 8. XPS analysis of white carbon layer.

Figure 9. XPS analysis of black carbon layer.

Figure 8 selects white carbon layer for XPS analysis, and Figure 9 selects black carbon layer for XPS analysis. According to the elements and components in the figures, the flame-retardant
mechanism of Nano flame-retardant samples can be inferred: Part of N and C elements in the coating react with oxygen to form nitrogen oxides and carbon oxides, and P element reacts with oxygen to form phosphorus oxides to stay in the carbon layer, which produces flame-retardant effect. The white carbon layer is nearly completely oxidized, and the proportion of O element is higher. The content of P element in the black area is higher than that in the white area, which indicates that the flame retardant effect in the black area is better; the complete combustion does not take place in this area, so the proportion of O element is relatively low. This may be due to the fact that the carbon layer density of the flame-retardant Nano sample is related to the fact that oxygen can only penetrate into the carbon layer one by one in the combustion state.

4. Conclusion
The following conclusions can be drawn through the study of Nano ultra-thin steel structure fire retardant coating and traditional fire retardant coating:

1. Compared with the photos after the test, it can be seen that the Nano coating has a large number of bubbles with small volume, dense and uniform arrangement, deep color of carbon layer, and no shedding phenomenon.

2. Compared with the cone calorimetric test data, it can be seen that the Nano coating can form a carbon layer with better thermal insulation performance in the combustion process, delay the ignition time of the coating, and reduce the heat release rate, total heat release and smoke production rate.

3. Compared with the scanning electron microscope, it can be seen that the carbon layer structure of the traditional coating is not dense enough, there are many holes in the carbon layer, and obvious honeycomb structure in the hole; but the carbon layer structure of the Nano coating is more complete and dense than that of the traditional flame retardant samples.

4. XPS energy spectrum analysis of the Nano coating shows that the content of O element is low in the black region of the sample after combustion, while the content of P element is high, indicating that the combustion in this region is not complete and the flame retardant effect is obvious.

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