The Analysis of the Application of Using Nanoceramic Oxides in Fire-resistant Coatings

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Abstract. The increased demand for enhanced fire safety in various industries has spurred interest in the properties and applications of nanoceramic oxide materials. This paper provides a thorough examination of the fundamental attributes of nanoceramic oxides, showcasing their exceptional temperature, corrosion, and wear resistance. The paper discusses synthesis methods like evaporation condensation, high-energy mechanical ball milling, and both vapor and liquid phase chemical techniques. The paper further explicates the underlying mechanisms that enable fire-resistant coatings to retard flames, highlighting thermal insulation, intumescence, and more. Of significance is the potential of nanoceramic oxides to augment the performance of these coatings, evidenced by applications like tunnel fire retardant coatings and steel structure coatings that integrate materials such as Mg $(OH)_2$, nano-SiO_2, and TiO_2. While challenges in raw material sourcing, eco-friendliness, production, and expertise arise, solutions are proposed. Conclusively, the study underscores the transformative potential of nanoceramic oxides in the realm of fire-resistant coatings, pushing boundaries in fire safety across sectors.

Keywords: Ceramic oxide materials, Fire resistance materials, Nanomaterials.

1. Introduction

The nanoceramic oxides is a kind of material that emerged in recent decades. The definition of nanoceramic oxides is oxidized ceramic materials whose inner pores reach nanoscale levels. Fire-resistant coatings are coatings capable of performing a fireproof and heat-insulating function. The basic technique of producing fire-resistant nanoceramic paint is to add nanoceramic powder to the basis so the paint layer can have better quality in heat insulation and flame retardant.

Fire-resistant nanoceramic paint can effectively reduce production costs and improve the efficiency of the machine. Oxide ceramics have great strength, high-temperature resistance, strong oxidation resistance, stable chemical properties, strong electrical insulation and many other good properties. Nanoceramics have a relatively low environmental impact, so the application is very promising. With the improving preparation methods and the development of new materials, nanoceramic oxides is certain to have enhanced structural stability and strength.

The passage will discuss outstanding abilities of nanoceramic materials, and the current application of the material. The writer would also simply describe future research work in the field of nanoceramic and reflections of drawbacks for present products.

2. An overview of the nanoceramic oxides

Oxide structure ceramics are a kind of widely used ceramic materials, generally means various oxide ceramics with a melting point higher than the melting point of SiO_2 crystals (1730℃), such as TiO_2, Fe_2O_3, SnO_2, SiO_2, Al_2O_3, ZrO_2, etc. [1] In the microstructure of nanoceramic oxide materials, the grain size, grain boundary width, second phase distribution, pore size and defect size are all below 100nm [2]. Oxide-structured ceramic materials have excellent chemical properties, such as high-temperature resistance, corrosion resistance, wear resistance and high stability. Compared with traditional ceramics, nanoceramics have better ductility, similar to metal.

In recent years, many methods have been found to prepare nanoceramic oxide materials, which can be divided into physical preparation methods and chemical preparation methods. Among the

physical preparation methods, the most commonly used technology is the evaporation condensation method [3]. Its working principle is to fill a vacuum evaporation chamber with low-pressure noble gases, making atoms of which collide with the atomic fog generated by the evaporation source or heating metals and compounds, thereby losing energy and condenses into nano-sized clusters. The clusters aggregate on the liquid nitrogen cooling rod and eventually form nanoparticle powders. Another physical preparation method is the high-energy mechanical ball milling method [4]. The basic working principle of the method is to obtain nanocrystals through mechanical friction. The details include placing the powder in a closed container so that it produces ultra-fine particles with the rotation or shaking of the container. In addition, there are other techniques, such as mechanical grinding and explosion [5].

As for chemical preparation methods, a common method is called the vapor phase chemical method [6]. The basic principle of the method is to make the reaction product vapor form a highly over-saturated vapor pressure under conditions much higher than the critical reaction temperature calculated by thermodynamics, then automatically condense to form a large number of crystal nuclei. These crystal nuclei will continuously grow and aggregate in the heating zone, and stop growing and crystallizing when entering low-temperature zones. Finally, the nanoceramic powder will be obtained in the collecting room. The gas phase chemical synthesis can be further divided into resistance method [7], plasma method [8], laser method [9] and electron beam method [10] according to the different heating sources. In particular, laser-induced vapor deposition uses reaction gas molecules to absorb a specific wavelength of the laser beam, thereby triggering a variety of laser-induced chemical reactions and forming ultrafine powder. Also, liquid-phase chemical methods are used to synthesize powders through the liquid phase, including precipitation, sol-gel [11], spray pyrolysis, and hydrothermal synthesis. For example, the precipitation method is to get the ceramic precursor precipitate by adding a precipitating agent to the metal salt solution and then get the nanoceramic powder by burning. The sol-gel method is to dissolve the alkoxide in the organic solvent by adding distilled water to form sol, which then changes into a gel. Nanoceramic powder can be obtained after low-temperature drying and high-temperature forging. The method of spray pyrolysis is to spray the metal salt solution into the high-temperature atmosphere in a fog to directly obtain the oxide nano powder or form the powder after subsequent heat treatment. Each of these methods has its own characteristics and applications, providing a wide range of choices for the preparation.

3. Fire-resistant coatings Materials

Fireproof coating is a kind of special coating used for flammable surfaces, reducing the flammability of certain surface, blocking the spread of the fire, preventing the spread of the fire and isolate the fire source, in order to extend the time of the substrate to catch fire or increase the adiabatic performance, and improve the fire resistance quality of the coated material. The fireproof coating is on the surface of the materials, in addition to flame retardant, also has the properties of rust prevention, water and heat resistance, corrosion prevention, coating toughness, coloring, adhesion, easy drying and certain gloss [12].

3.1. Mechanisms of the fire-resistant coating materials

The efficacy of fire-resistant coatings is a culmination of several intricate mechanisms that work in tandem to protect the substrate from the detrimental effects of fire. Central to the function of many fire-resistant coatings is their capacity for thermal insulation. When exposed to high temperatures, these coatings form a protective layer, often swelling or expanding in a process known as intumescence. This layer serves as a thermal barrier, effectively shielding the underlying material from the intense heat of a fire. Additionally, certain coatings can reflect a significant portion of the heat, much like how a mirror reflects light, further preventing the substrate from reaching ignition or degradation temperatures. Further, when subjected to fire, some coatings undergo a process that results in the formation of a dense, carbon-rich protective layer known as char. This char is pivotal in

thwarting the fire's progression, acting as a physical barrier between the flame and the substrate. Furthermore, the stability of the char is crucial; a stable char will maintain its structure and integrity even under prolonged exposure, preventing the flame from penetrating and reaching the underlying material. Another notable mechanism employed by fire-resistant coatings is the release of non-combustible gases upon heating. As the coating decomposes under the influence of fire, it releases gases such as water vapor, carbon dioxide, and other inert gases. These gases play a dual role: firstly, they dilute the concentration of flammable gases in the vicinity, making it harder for the fire to sustain itself. Secondly, their release can create a 'puffing' effect, pushing the flames away from the substrate, further insulating the material from the fire's heat and potential damage.

3.2. Main components and types of fire-resistant coatings

Fire retardant coatings are generally composed of synthetic non-burning or difficult-to-burn organic polymer resin as the main body. The organic polymer resin is modified specially, and appropriately add a small amount of flame retardants, blowing agents, carbon sources and other components to form a fire protection system. According to the different uses, objects can be divided into: decorative fireproof coating, cable fireproof coating, steel structure fireproof coating, prestressed concrete floor fireproof coating and some other kinds.

In addition, fire-resistant coatings encompass a diverse array of materials, each tailored to offer optimal protection against fire. Inorganic compounds, such as silicates, alumina trihydrate, and magnesium hydroxide, inherently resist combustion due to their mineral composition. Intumescent materials like ammonium polyphosphate, melamine, and pentaerythritol swell when exposed to fire, forming a protective char barrier. Organic compounds, on the other hand, include flame retardants such as halogenated and phosphorus-containing compounds that inhibit or suppress the combustion process. Additionally, nanocomposites, including layered silicates, carbon nanotubes, and graphene, are being increasingly employed due to their enhanced fire-resistant properties at the molecular level, adding a modern edge to the age-old challenge of fire protection. Nano oxides have garnered significant attention in recent years due to their potential to improve the fire resistance of various materials. The nano-scaled size of these particles allows for enhanced interaction with polymers and other substances, and their intrinsic properties confer unique fire-resistance capabilities.

3.3. Performance evaluation indicators of fire-resistant coatings

The evaluation methods and standards of fireproof coatings are various. The industrial fire-resistant coatings for coating finishes are graded according to GB/T1544 42.1-95 "Gradings for Decorative Fireproof Coating". The fire resistance time (min) was detected according to GB/T154 42295 "Fire resistance test method for fire retardant coatings - large plate burning method". The flame spread ratio was tested according to GB/T1544 42.3-95 "Test method for fire resistance of fire-retardant coatings - tunnel burning method". The quality (g) loss and carbonation volume c (m3) of the coating was detected according to GB /T15 Soul 4, 2.4-95 "Test method for fire resistance of fire-proof coatings - chamber burning method".

Since structural fire-retardant coatings have differences in water-based and oil-based points, and also in thick coating type, thin coating type and ultra-thin type. Fire-resistant coatings for steel structures are tested and graded according to GB14907-94 "General Technical Conditions for fire-resistant Coatings for Steel Structures" and GB99788-88 "Fire-resistant Test Method for Building Components".

Fire retardant coatings for wire and cable shall be tested according to GB1266.0590 “Burning test method for bundle wire and cable”. After the fire source is removed, and when the source can self-extinguish, the residual growth of qualified wires is over l m.

4. Application of Nanoceramic Oxides in Fire-Resistant Coatings

4.1. The role of nanoceramic oxides in improving the performance of fire-resistant coatings

Nanoceramic oxides have high heat resistance, good oxidation resistance in high temperatures, low density, high fracture toughness, corrosion resistance and wear resistance. Nano-silica and other oxides can be ceramic in the burning process. The dimensional stability before and after burning is better, as well as mechanical properties, compared with the common fireproof silicone rubber coating system [13]. Nanometer ceramic coating is a coating treated by nanotechnology, and has excellent adhesion and strong wear resistance. At the same time, the nanoceramic oxides coating has excellent temperature resistance, which improves the high temperature oxidation resistance after film formation. At the same time, the porosity of nanomaterials can improve the strength and toughness of the coating, preventing high temperature cracking, improving the density of the carbonized layer after the fire expansion of the coating, therefore improve the fire resistance of the coating.

4.2. Application cases of nanoceramic oxides in fire-resistant coatings

Flame retardant system material is the core of fire-retardant coating, and it has great influence on fire retardant coatings. Currently, there is a tunnel fire retardant coating that uses Mg (OH)2 as an auxiliary agent. After the high temperature, the coating can decompose non-toxic noble gases and absorb heat by thermal decomposition and phase transition. The surface layer can gradually form a carbonization layer and then an expanded foam layer, reducing heat conduction and the rate of component temperature rise effectively. The coating has properties, such as fire resistance, high adhesion, good water resistance, environmentally friendly and so on.

The addition of nano-SiO_2 [14]and TiO_2 can improve the strength of the carbon layer [15] and extend the fire resistance limit of the steel structure. When 1.5% (mass fraction) of nano-SiO_2 is added, the limit can reach 110min. Nanoceramics can strengthen the polymer, and because the nanoparticles are small. The particles have characteristics of great strength, toughness and stability at high temperatures, also improving the thermal stability of the coating. However, the pure preparation of nano-SiO_2 has a large amount of various hydroxyl groups on the surface, appearing to be polar and has strong hydrophilicity. It is difficult to evenly disperse the particles in the organic polymer during the application process, thus the nano effect of the particles is unlikely to be shown. How to disperse nano-SiO_2 evenly in materials to improve the properties of composite materials is a difficult problem faced by many scientists. The thermal decomposition temperature of HYO coating is 290℃, and that of HY3 coating is 359℃, which is 69℃ higher than that of HYO coating [16]. The thermal decomposition temperature of H coating is 376~C, which is 86℃ higher than that of HYO coating. Obviously, the epoxy silicone heat-resistant anticorrosive coating prepared by adding modified nano-SiO_2 has a higher heat resistance temperature than the silicone resin varnish. This is because the nanoparticles are small, and they have high strength, toughness and temperature stability at high temperatures. Therefore, nanoparticles can improve the thermal stability of the coating. The ceramic powder makes the thermal stability of the coating further improved. This is because the organic groups and the main chain of the resin base are destroyed at high temperatures, forming an active center at the broken place also forming a dense enamel-like coating with the melted ceramic powder. The final product can withstand higher temperatures [17].

4.3. Challenges and solutions of applying nanoceramic oxides in fire-resistant coatings

The current nanoceramic oxide materials [18] do not have a great market price because of preparation technology. For instance in the Chinese market, compared with traditional coatings, nanoceramic oxides, as an emerging industry, the price is relatively high. Moreover, the channel of selling is limited, and the sales are difficult to increase rapidly. considering of its complex technique and the difficulty of standardized construction, training for manufacturing is difficult. As result of the lack of professionals, the sales and promotion of nanoceramic oxides will be limited. Based on the analysis above, the future development of nanoceramic oxides includes the following four points:

(1) Development of raw material suppliers. The continuous development of raw material suppliers will help reduce the prices and improve the quality, making the products conducive to the large-scale development.

(2) The improvement of environmental friendliness. With the increase of utilization, the efficiency and environmental friendliness requirements would increase.

(3) Optimization of production process. The optimization of construction technology and simpler construction are helpful to the training of workers.

5. Summary

Nanoceramic oxides have excellent bonding and mechanical properties. The material is corrosion-resistant and heat-resistant. Nanoceramic oxides can be used as coatings and adhesives, widely used in aerospace, electronics, engineering, civil construction and other goods. The application of paint ranks first among all the possibilities. The current fireproof materials must meet the requirements of both flame retardant and environmental protection. The development trend of low smoke, low toxicity and no halogenation is clear. Ceramic able polymer composites are made of green, non-toxic and pollution-free materials. These materials can maintain good elastic and mechanical properties of polymer at room temperature. When the material encounters fire or is in a high-temperature environment, it can be transformed into a self-supporting hard ceramic body. The ceramic bodies can better maintain the original size and shape of the composite material. The intact ceramic layer has good fire resistance, helping to cut out the transfer of combustibles and heat, and further inhibit the loss of the material in the inner layer of the composite material. Therefore, the mechanical properties and dimensional stability of ceramic able coating materials before and after combustion is critical to fire resistant properties.

In the future, fireproof coatings and the entire coating market will go to the direction of energy saving, environmental protection, low cost and high performance. With the application of organic synthetic materials, the combustibility problem is becoming concerning. Halogen-containing organic polymers often lead to the deterioration of material properties, shortening of stability and increasing prices. The method of fire-resistant coating on the surface can not only maintain the excellent properties of original organic synthetic materials but also be applicable economically. In addition, the application of fireproof coatings on organic synthetic materials is promising as well.

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