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Surface Curing and Properties of Titanium Dioxide Self - Cleaning Ceramics

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ABSTRACT
In this paper, the curing mechanism of TiO2 photocatalytic film on the ceramic surface is introduced, and the relationship between photocatalysis, hydrophilicity and self-cleaning properties of TiO2 ceramics is analyzed. Finally, the mechanism of antimicrobial properties of TiO2 ceramics and its relationship with temperature were analyzed.
KEYWORDS: titanium dioxide; self-cleaning ceramics; curing mechanism; photocatalytic; hydrophilicity; antibacterial

1. Introduction

Photocatalytic self-cleaning ceramics are widely used in building walls, kitchen walls, hospitals, tableware and other fields, which come with photocatalytic sterilisation, degradation of organic pollutants and super-hydrophilic and other functions, [1]. Among the photocatalysts, TiO2 semiconductor catalysts have been widely used because of the good chemical stability, safety, non-toxicity, high photocatalytic activity and low preparation cost. It is an ideal photocatalytic self-cleaning ceramic preparation material [2].

2. TiO2 photocatalytic ceramics

Self-cleaning ceramics with the TiO2 catalyst can be divided into two types according to the preparation process [3]: For the first type, TiO2 powder is added in the ceramic glaze, and then sintered by ceramic preparation process to get self-cleaning ceramic. Due to the physical and chemical properties of the ceramic glaze itself, the addition of TiO2 catalyst in the ceramic glaze is minimal, and the ceramic sintering temperature is very high (1100 ~ 1300 ℃). TiO2 is transformed from anatase with high photocatalytic activity to less active rutile type, which greatly reducing the photocatalytic activity and bactericidal effect [4]. Therefore, this technology is less attractive for development. The second type is the ordinary glazed ceramic surface coated with a TiO2 film. The process uses butyl phthalate as the main raw material, while the ordinary ceramic is immersed in titanium solution. A gel film will be formed after a certain rate of pulling, ageing and drying. Finally, the surface of TiO2 thin film ceramic will be obtained after high-temperature annealing [5]. The surface TiO2 coated thin film technology avoids the crystal transition of TiO2 at the sintering temperature of the ceramic, which provides the advantages of thickness controllability and simple preparation process. It becomes an aroused general interest in the field of environmental catalysis point [6].

In the late 1980s, Japan's TOTO company developed TiO2 photocatalytic antibacterial sanitary ceramics which had TiO2 film coating. These ceramics had been used in hospitals and other places which required a high standard of sanitary. Subsequently, some ceramic technology workers began to use the latter method to develop photocatalytic antibacterial glazed tiles [7]. The surface of the film is prone to have 'rainbow effect', along with poor adhesion and easily fall off. The production cost is expensive with high energy consumption, which leads to difficulty for industrial production [8]. Spray pyrolysis is a new type of thin film preparation technology, which does not require expensive vacuum equipment and target material. The simple experimental conditions, low cost and good film adhesion provide significant advantages to the large-scale industrial production. However, the traditional spray pyrolysis method uses an spray gun atomization way, which high-pressure carrier gas will break the liquid into droplets, and to be carried to the heated substrate for thermal decomposition [9]. During the atomization process in the nozzle, the efficiency of atomization is low with contamination from impurities, along with poor control of atomization particle size, uneven film surface and other defects [10]. An ultrasonic spray pyrolysis technology uses ultrasound to break liquid into fine droplets, which together with gas to form aerosols, subsequently will be sent to the reaction chamber pyrolysis film. The process occurs at high atomization rate with small, uniform particles, and the composition can be easily controlled with low impurities to form a film in a single round.

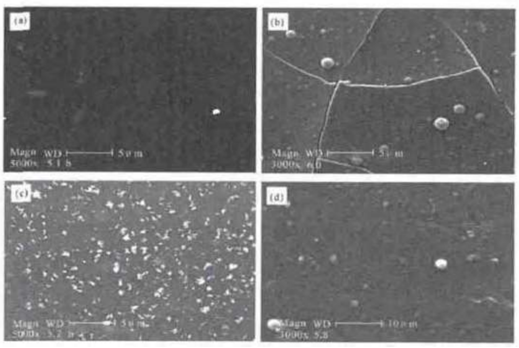
TiO2 has been gaining attention as it has good catalytic performance, chemical stability, non-toxic characteristic with abundant resource and low cost. TiO2 film or powder under ultraviolet (UV) irradiation will trigger production of electron-hole pairs, holes and water reaction to generate active hydroxyl (OH-), electron and superoxide radicals (O2-). The OH- and O2- degrade TiO2 organic matter to achieve photocatalytic purposes. This photocatalytic effect has been applied in a wide range of applications such as air purification, wastewater treatment and other environmental areas. In addition to TiO2 photocatalytic activity, the photo-induced hydrophilic effect in recent years has attracted more attention. Under an ultraviolet radiation, TiO2 surface turns into a highly hydrophilic characteristic, which provides anti-fog and automatic cleaning features. Although the TiO2 film has good super hydrophilicity under the UV irradiation, its surface returns to the hydrophobic state in the absence of UV for a period, which is not conducive to practical application. TiO2 and SiO2 composite film can effectively improve the super-hydrophilic effect of the film, which is mainly due to the SiO2 material are easy to form a thick physical adsorption of water on the surface. The presence of the light turns the film surface turns easily to hydrophilic properties and can prevent the oxygen adsorption on the surface, so that chemical adsorption of water to oxygen replacement slows down, thus extending the duration of super-hydrophilic characteristic.

3. Solidification Mechanism of TiO2 Photocatalytic Thin Films on Ceramic Surface

Previous studies showed that the super-hydrophilicity has a great influence on the self-cleaning of the TiO2 photocatalytic film [11]. The wetting angle of the TiO2 film on the surface is gradually decreased to 0 ° under UV irradiation. This phenomenon is called photo-induced super-hydrophilicity of the TiO2 thin film. By changing the microstructure of the TiO2 thin films, such as controlling the preferential orientation of crystal growth could improve the roughness and the super-hydrophilic TiO2 film.

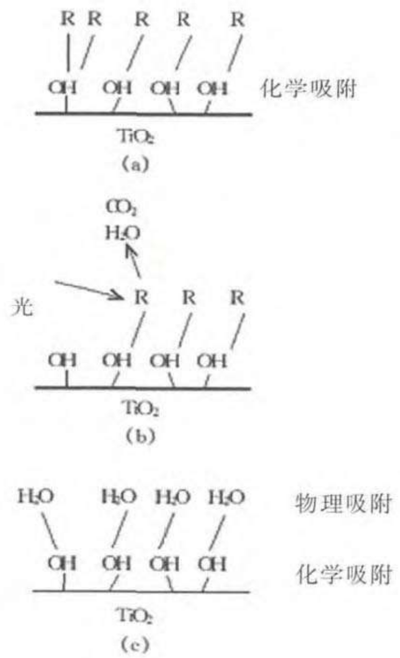
The photocatalytic activity of TiO2 can be enhanced by doping or photo-sensitizing TiO2. The incorporation of cerium nitrate can improve the degradation rate of the film, which is most significant when the mole fraction of cerium nitrate is 10%. At the same time, the introduction of iron nitrate with a mole fraction of 15% can make the utilisation rate of the film reach the extreme value, and the degradation rate of methyl orange is the highest. The result of lattice doping transition metal ions is to produce an internal bandgap in the TiO2 band, which is less than the wide band gap of TiO2 that can induce the absorption of visible light and improve the activity of the catalyst [12].

There are three kinds of crystal form for TiO2 photocatalyst in the usual state: anatase crystal, rutile crystal and brookite crystal. The anatase type has the strongest super-hydrophilic properties and photocatalytic activity. The titanium-crystalline type has weak hydrophilicity and photocatalytic activity. The rutile crystal type has no super-hydrophilic property and photocatalytic activity with high-temperature phase, while anatase and brookite are the low-temperature phases of TiO2. The transition temperature of Nano-TiO2 powder anatase to rutile type is changed at the about 600 °C, which the transition form is irreversible. Different glaze bearing the temperature is different. When the temperature is further increased, the glaze can be melted, resulting in the wrapping of titanium dioxide, depression and the reaction with glaze subsequently leads to the loss of activity. Also, the glaze composition will also affect the photocatalytic activity of TiO2 film [13]. The photocatalytic activity of TiO2 thin films of glazed ceramics and glazed ceramics is also significantly different, and the photocatalytic activity of TiO2 thin films is reduced by the infiltration of the glazed ceramic matrix [14].



Rutile TiO2 surface adsorption of organic matter and oxygen capacity is not as good as anatase, due to smaller surface area, photoelectrons and holes which causing easy composition and affecting the catalytic performance. It was found that the super-hydrophilic and photocatalytic activity of TiO2 photocatalytic materials were proportional to their specific surface area. The key to developing self-cleaning ceramics with high-surface-area, high hydrophilicity and photocatalytic activity of anatase crystalline TiO2 photocatalytic materials are dependent on the stability of this material coated on the ceramic surface.

In the current development, the simple and easy way to apply TiO2 photocatalyst fixation method is to prepare active TiO2 powder mixing with the solvent and flattening film with the spray method, dipping method or film coating method. After coating to the ceramic surface, and the dry sintering process transforms the ceramic with the solid film. For the solvent selection, the volatility is a general consideration factor, which will promote the evaporation and drying of the film. The solvent used in the present is usually an organic solvent such as water or isopropanol, and the organic functional group can replace the hydroxyl group on the surface part and play a certain steric hindrance to reduce or prevent the occurrence of agglomeration.



The purpose of immobilisation is to ensure that the photocatalytic activity under the premise of the carrier and TiO2 to produce a binding force between, to avoid the precipitation of TiO2 photocatalytic failure, hence the fastening fastness is a very important quality parameters. The photocatalytic activity of TiO2 photocatalytic film is combined with the carrier, and the photocatalytic activity can be maintained for a period. By increasing the sintering temperature, or doping SiO2 component in the TiO2 photocatalyst, this forms a solid TiO2 / SiO2 supported catalyst with greater carrier bonding strength in the presence of Ti-O-Ti bond, and Ti-O-Si bond, in the TiO2 film.

With the increase of sintering temperature, the crystal size increases, the structure tends to be intact. While the stress and strain between crystals become smaller, the adhesion strength increases. It is also possible to improve the durability of the film by using a layered sintering process which is sintered at one time per layer. The results show that the longitudinal shrinkage of the wet film is greater than that of the surface during the drying process. The surface of the film is prone to microcracks, the multilayer microcracks accumulate, and the film is sintered. After the phenomenon of shedding, but the film is easy to produce 'iridescence' phenomenon. Fig.1 shows the SEM images of TiO2 films prepared by blank glazed ceramics and different deposition temperatures. As can be seen from Figure 1, the surface of the blank glazed ceramic (a) is very smooth, fewer impurities. When the deposition temperature is at 300°C, no crystal appear, and there is a crack (b). This may be due to the low deposition temperature, the weak diffusion of atoms, the absence of sufficient polymerization, the film has not been fully crystallised, while the inner and outer layers of the film produce uneven thermal stress, leading to film surface cracking. When the deposition temperature is at 350 ℃, the crystal surface of the ceramic appears, the distribution is more uniform (c) because the spray time is short, the particle density is low. When the deposition temperature is increased to 400 ℃, the crystal grain on the surface of the film tends to increase, but the crystallinity is not obvious (d). The reason is that when the temperature rises, the uniform fine atomised particles have evaporated before reaching the ceramic substrate, but have not yet reached the solid sublimation temperature, hence cannot be nucleated on the ceramic growth, but only the individual large particles can be crystallised. Therefore, the deposition temperature of the film is a very important preparation condition, extreme high or low temperature is not the ideal condition for film forming.

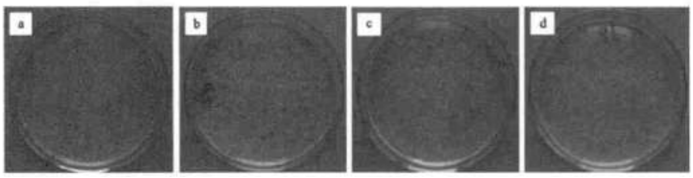
4. Photocatalytic, Hydrophilic and Self - cleaning Properties of the TiO2 Ceramics

TiO2 film and its composite film for glass and mirror surface can play a transparent, anti-fog and self-cleaning feature, while a very good hydrophilicity of the surface is the key to self-cleaning film, that is, water droplets on the surface replace the surface of organic matter adsorption and wash away organic dirt. The hydrophilicity of TiO2 is due to the change of its surface structure, that is, under the condition of ultraviolet light irradiation, the TiO 2 is excited to the conduction band, the electron-hole pairs are generated on the surface, and the Ti4 + on the surface of TiO2 is reduced to Ti3 +. The oxygen ions in the air are adsorbed in the oxygen vacancies and become chemically adsorbed water (surface hydroxyl groups), so the surface of the TiO2 exhibits hydrophilic characteristics. When the UV light irradiation is stopped, the chemical adsorption of hydroxyl is replaced by the oxygen in the air, and returns to the hydrophobic state. Also, the hydrophobic organic matter adsorbed on the surface of the film will also cause the surface transition from a hydrophilic state to a hydrophobic state [15].

Hydrophilic TiO2 film surface self-cleaning mechanism can be shown in Figure 2. The surface of the film absorbs water. When a few hydrophobic molecules attached to the chemically adsorbed water of TiO2 are decomposed into H2O, CO2 and inorganic matter, the surface of the inorganic matter are easily washed away by water. The chemical adsorption of TiO2 will also adsorb a layer of physical adsorption water by Van der Waals force and hydrogen bonding. The surface of the film will always maintain a thin layer of the water film. Even if the organic soil is deposited on the surface, the water film can disrupt the direct contact of the film surface with TiO2. Because the organic dirt and the film do not form a strong combination of the surface, the dirt can be easily washed away in the absence of light. Therefore, the super-hydrophilic surface can be complementary with its photocatalytic activity, and both together to make the film surface to achieve the self-cleaning effect. A single photocatalytic or single hydrophilic property does not allow the surface to maintain its self-cleaning for a long time, and only the two synergies can maintain the surface self-cleaning effect. Photocatalytic decomposition of the surface of the organic pollutants can be decomposed into H2O and CO2, with self-cleaning function, and other hydrophobic organic molecules to help restore the surface of the hydrophilic, easy to clean the surface and maintain self-cleaning function.

When the semiconductor TiO2 and the insulator SiO2 composite often produce some special properties, especially the changes in acidity because the hydroxylated semiconductor surface and acid have a greater relationship. In fact, the composite oxide exhibits a higher acidity than the single constituent oxide. When the two component oxides are complexed together, the new acid sites are formed due to the coordination of the metal ions and the electronegativity. The addition of SiO2 improves the photocatalytic activity of TiO2 film, which is mainly due to the addition of silicon to increase the surface acidity of the TiO2 film. In the binary system of oxide, SiO2 and TiO2 form Lewis acid, the surface of the acidity not only in the form better adsorption sites, but can form strong hydroxyl groups on the surface. These hydroxyl groups act as trapping sites for holes, preventing the recombination of electron-hole pairs, resulting in strong oxidative activity of hydroxyl groups that increase the photocatalytic reaction.

When the surface of TiO2-SiO2 is strong Lewis acid, due to the cation which has a high electron affinity, it can firmly grasp the OH-ions in the water, so the water H + ions are easily combined with the surface of the oxygen ions on the surface to form more hydroxyl groups. The addition of OH-ions on the surface is easy to combine with the photogenerated holes. As the hole capture sites, not only the effective separation of the electron-hole pairs is promoted, but also the strong hydroxyl groups of the active hydroxyl groups are enhanced to improve the photocatalytic reaction.



The adsorption of H2O molecules in the air is enhanced by the surface acidity enhancement, and the adsorption capacity of the pollutants in the air is relatively weak during the competitive adsorption process. Therefore, with the increase of SiO2 content, the surface adsorption of organic matter decreased. The surface-stabilized chemical and physical adsorption of the aqueous layer stabilises the Ti3 + -OH structure on the TiO2 surface, allowing the TiO2 surface to maintain long-term hydrophilic properties in the absence of light. Also, in the TiO2-SiO2 binary system, the interaction and substitution of titanium and silicon atoms in different coordination states can stabilise the Ti-O structure and inhibit the crystal formation. Crystal refinement gives it a greater quantum size effect. However, when the content of SiO2 is too high, the surface is occupied by more SiO2, the effective surface of TiO2 is reduced, and the electron-hole pair is not easily induced by light excitation. Therefore, the super-hydrophilicity and photocatalytic activity decrease and the self-cleaning effect are weakened.

5. TiO2 ceramic antibacterial properties

Figure 3 shows the antimicrobial effect of titanium dioxide film self-cleaning ceramics at 15 min in the presence of near-ultraviolet light at different treatment temperatures, and gradually increased from a ~ d temperature. It can be observed from Fig. Three that the number of bacteria in the bacterial solution decreases first with the increase of the heat treatment temperature. This shows that titanium dioxide film self-cleaning ceramic at the appropriate heat treatment can be achieved better with an antibacterial effect.

The bacteriostatic rate of the titanium dioxide film self-cleaning ceramic was determined by the method of plate colony counting under the observation of the biological microscope, and then calculate the inhibition rate of E.coli on titanium dioxide film self-cleaning ceramics. The experimental results are shown in Table 1. In Table 1, at near ultraviolet light irradiation 120 min, the bacterial survival rate is still high for the control group (blank ceramic), the inhibition rate was 32.47% with UV sterilisation; while the antibacterial rate were more than 70% when the bacteria was placed in titanium dioxide film self-cleaning ceramic. When the ceramic was sintered at 500 ℃ heat treatment, the antibacterial rate was up to 98.42%. With the increase of heat treatment temperature, the inhibition rate of titanium dioxide film self - cleaning ceramics increased first and then weakened. This is mainly due to the heat treatment temperature is conducive to the formation of anatase phase titanium dioxide, antimicrobial properties, but the high heat treatment temperature so that glazed ceramic substrate Si4 +, Na + and other elements diffused into the titanium dioxide film to form oxides Anatase phase titanium dioxide film crystallization cannot be improved, therefore the antibacterial properties decreased in the presence of mixed crystal [17]. Especially when the Na2O content of more than 10% will critically reduce the titanium dioxide photocatalytic activity and antibacterial ability. The effect of the crystal form of titanium dioxide on its performance is the main effect, and the heat treatment temperature of 500 ℃ is an excellent performance of the anatase phase titanium dioxide film self-cleaning ceramic.

Titanium dioxide photocatalytic inhibition mechanism is an indirect reaction [18]. The titanium dioxide catalyst is a semiconductor with a band gap of 3.2 eV, which itself is non-toxic and killing against microbial cells. When it is irradiated with ultraviolet light with a wavelength of less than 386 nm, the electrons in the valence band are excited to the conduction band, resulting in a highly active electron e- and a positively charged hole h + on the valence band, resulting in the formation of highly active electron-hole pairs on the semiconductor surface [18,19]. (OH), photogenerated electrons, react with oxygen molecules to form superoxide radicals, and further form hydroxyl radicals (· OH), which reacts with H2O or OH- on the surface of the catalyst to form strong oxidising hydroxyl radicals (· OH) OH) and H2O2 and other reactive oxygen species [20]. These reactive radicals have a strong reactivity and oxidative ability to kill bacteria by oxidising the coenzyme A in the bacteria, destroying the cell wall (membrane) permeability of the bacteria and the structure of the DNA, and interrupting the electron transport.

Bright time/min	Anti-bacteria/%				
	Blank place	T-0 ℃	T-450 ℃	T-500 ℃	T-550 ℃
30	15.56	43.79	50.52	65.28	56.52
60	21.28	56.49	65.64	82.54	70.36
90	27.51	67.36	78.81	95.77	82.34
120	32.47	73.84	90.63	98.42	94.58

6. Conclusion

Titanium dioxide photocatalyst coated on the surface of ceramic (glass) made self-cleaning functional ceramics (glass). However, due to the low temperature of the glass making, the use of TiO2 film and ceramic (glass) surface adhesion is not strong enough. The fast decreasing rate of photocatalytic activity and poor durability impact the use of the product. The film can be improved through the improvement of adhesion. Improved measurements: 1) to improve the baking (sintering) temperature, in control of lower than the TiO2 anatase crystal to rutile type transition temperature, maintaining the premise of photocatalytic activity, at high-temperature sintering as possible, making the film and carrier of the binding state from the physical adsorption to the chemical bond of the strong bond; 2) doped, the preparation of supported catalyst. TiO2 photocatalyst doped with SiO2 components to form a solid supported catalyst, the film has both Ti-O-Ti bond, and Ti-O-Si bond, the film bonding strength will increase tremendously, while doping another Metal ion can significantly improve the photocatalytic ability of the film; 3) layered sintering process to solve the monolayer film which is too thick, the longitudinal shrinkage is greater than the surface adsorption force, micro-cracks cumulative stacking, affecting the film firmness of the problem.

To improve the practicability of TiO2 photocatalytic ceramics, it is necessary to enhance its photocatalytic activity, expand its excitation wavelength range and enhance the adsorption capacity of photodegradants. The photocatalytic activity of TiO2 depends on the number of electron-hole pairs involved in the carrier transfer reaction on the interface.

Therefore, to strengthen the carrier on the interface transfer reaction, there is a need for modification of TiO2. To improve the quantum efficiency, the photogenerated electrons can be captured by adding appropriate surface defects to separate the photo-generated electrons and holes, thereby reducing the recombination probability of the two. One of the effective ways to control surface properties is a semiconductor noble metal deposition. If the Rt is deposited on the TiO2 surface to improve the activity, the deposition of the noble metal on the TiO2 surface could be carried out by ordinary impregnation-reduction. Also, the light reduction can also be used. The most commonly used deposition of precious metals is Group VII of Pt, followed by Ru, Au, Ag, Pd, etc., the deposition of these precious metals generally improve the photocatalytic activity of TiO2.

In recent years, the researchers began to mix TiO2 with building materials or coat it on the ceramic surface and developed new TiO2-based functional materials. The addition of TiO2 in the building materials enables clean air, sterilisation, self-cleaning, anti-fog and other functions, such as building cooling. Due to the unique optical properties of TiO2, the building materials also have a decorative effect (Ceramic tile, glass, paint, aluminium alloy panel, plastic, etc.) moreover, the traffic (wall, glass, paint, etc.), the application of the new materials and building materials (tunnel walls, noise walls, floor tiles, traffic signs, street lamps, etc.).

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