Low temperature deposition and characterization of TiO$_2$ photocatalytic film through cold spray

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Received 7 August 2007; received in revised form 17 December 2007; accepted 17 December 2007

Available online 23 December 2007

Abstract

Cold spray was employed as a novel low temperature approach to deposit titanium dioxide (TiO$_2$) photocatalytic film. The film microstructure was characterized using X-ray diffraction and scanning electron microscopy. The photocatalytic performance was examined through acetaldehyde degradation under ultraviolet illumination. Results showed that TiO$_2$ film was successfully deposited on substrate surface through cold spray. The film thickness reached up to 15 $\mu$m. The film presented a rough surface and porous structure. Owing to the low temperature of spray powder, no phase and particle size changes occurred to TiO$_2$ during deposition. It was found that the cold-sprayed TiO$_2$ film was active for photodegradation of acetaldehyde.

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Keywords: Titanium oxide; Film; Photocatalysis; Cold spray

1. Introduction

Titanium dioxide (TiO$_2$) is a promising photocatalyst owing to its potential applications to environmental purification, solar cells, sterilization, cancer therapy and antifogging films [1–5]. The immobilized TiO$_2$ photocatalysts in the form of films are practically of many advantages than that of powders [6]. Many coating processes were employed to deposit TiO$_2$ photocatalyst films. Those processes include two routes: (1) preparation from TiO$_2$ powders ready for use, e.g. the commercially available Degussa P25 titania powder, and (2) preparation of a photocatalyst in situ from a precursor [7,8].

As photocatalyst powders are deposited on an inert support, they are fixed on the support by some binders, such as glue and various solutions [6,9,10]. The adherence of the photocatalyst to the support is very important, since some catalyst particles may be detached from the support and enter the liquid phase if the adhesion of the photocatalyst to the support is not strong enough. Annealing treatment from 500 to 700 °C is often utilized to improve the adherence [6,9,10]. However, owing to the change of the surface microstructure of photocatalyst powders, the immobilization processing of photocatalyst powders at a high temperature generally deteriorates photocatalytic activity. Therefore, it is of significant importance to retain the photocatalytic activity of feedstock in the film. On the other hand, since the photocatalysis takes place on the external and internal surface of photocatalyst particles, the microporous film presents higher photocatalytic performance owing to its larger surface area than compact film. Consequently, film with micro-porosity or nano-porosity is of essential interest.

In this study, nanoporous TiO$_2$ film was deposited with TiO$_2$ powder through cold spray. The microstructure and photocatalytic performance of the deposited film was examined.

2. Experimental

2.1. Materials

TiO$_2$ powder in pure anatase crystalline structure was used as feedstock. The starting anatase powder (10–45 $\mu$m) was prepared through agglomerating ultra-fine primary particles
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(Ishihara ST41) with nominal size of 200 nm using polyvinyl alcohol as a binder. The morphology of the powder is shown in Fig. 1. The powder is of spherical morphology. Stainless steel plate with dimensions of 105 mm × 25 mm × 1.5 mm was employed as a substrate for film deposition. Prior to spraying, the substrate was blasted with alumina grits.

2.2. Deposition of the film

TiO$_2$ film was deposited using the cold spray system developed in Xi’an Jiaotong University. The setup of cold spray system has been described in detail elsewhere [11]. In this study, nitrogen was used as a driving gas with an inlet pressure of 2.0 MPa and temperature of 300 °C. Nitrogen was also used as the powder carrier gas. The stand-off distance of the sample from the nozzle exit was fixed at 10 mm. During deposition, the spray torch was manipulated by a robot (Motoman) and traversed at a relative speed of 500 mm/s over the substrate.

2.3. Characterization of the film

The topographical morphology was observed using scanning electron microscopy (SEM) (Hitachi S2700). The cross-sectional morphology was characterized using field emission scanning electron microscopy (FESEM) (JSM-6700F). The phase structure was characterized using X-ray diffraction (XRD) system (Rigaku D/max-2400). XRD analysis was carried out using Cu Kα radiation at 40 kV and 100 mA. Scan speed for 2θ was 2°/min during test.

An experiment setup was assembled to examine the photocatalytic performance of TiO$_2$ deposit by the photocatalytic decomposition of acetaldehyde under ultraviolet illumination. A quartz cuvette with the dimensions of $\Phi$ 26 mm × 220 mm was used as the photocatalytic reactor. A 20 W ultraviolet lamp with a dominant wavelength of 254 nm was used as illuminating source. The radiant intensity at the film surface was about 1 mW/cm$^2$. The acetaldehyde concentration in the cuvette was determined through using gas chromatography (Agilent 6890).

3. Results

Fig. 2 shows the topographic morphologies of cold-sprayed TiO$_2$ film and the starting powder. The film presented a rough surface morphology. The humps pointed out by the arrows shown in Fig. 2a were formed through the stacking of the deformed powder. The detailed examination of the surface morphology clearly showed that the surface structure (Fig. 2c) of the cold-sprayed film was similar to that of the powder (Fig. 2b). The size of primary particles in the film was observed to be 0.2 μm, which is the same as that in the starting powder. The film presented a porous structure, which was formed by the stacking of 200 nm particles. Fig. 3 shows the cross-sectional morphologies of the cold-sprayed TiO$_2$ film. It is clearly seen from Fig. 3 that a film with a thickness of 10–15 μm was deposited on the substrate surface. It was also found that in this case the thickness of the films could not build up further no matter how many passes the deposition was repeated for. Although the spherical powder was used as feedstock, the film consisted of two to three layers.

Fig. 4 shows the XRD patterns of the film and the powder for comparison. It can be seen that the film presented the same pure anatase phase as the powder. Clearly, the original crystalline structure of the powder was retained in the film. Moreover, several small diffraction peaks corresponding to the stainless steel substrate appeared in the XRD pattern.

Fig. 5 shows the chromatograms of gas samples taken from the photocatalytic reactor after the acetaldehyde gas had been photocatalytically degraded for different time. A peak at 122 s in the chromatograms represented acetaldehyde. It can be seen that the peak intensity decreased with the reaction time. In addition, a new peak appeared at 102 s in the chromatograms, the intensity of which tended to increase with the degradation of acetaldehyde. This may be attributed to one intermediate resulting from the decomposition of acetaldehyde. The change of the relative concentration of acetaldehyde with reaction time determined by quantitative analysis is shown in Fig. 6. For comparison, the change of the relative concentration of acetaldehyde with reaction time determined by quantitative analysis is shown in Fig. 6. For comparison, the change of the relative concentration of acetaldehyde with reaction time determined by quantitative analysis is shown in Fig. 6. Result of a HVOF-sprayed TiO$_2$ film with the same spray powder in this study at fuel gas flow of 24 l/min was also added in Fig. 6 for comparison.
It can be clearly seen that the decomposition of acetaldehyde took effectively place by the illumination in the presence of TiO\textsubscript{2} film. Only 15% acetaldehyde was decomposed by the UV light illumination in 30 min. On the other hand, when the cold-sprayed film was present in the reactor, over 55% and 95% of acetaldehyde was photocatalytically degraded in 30 min for HVOF-sprayed film and cold-sprayed film, respectively. This fact means that the photocatalytic degradation of acetaldehyde by TiO\textsubscript{2} catalyst is much more active than that by photolysis of UV light. Furthermore, the activity of the cold-sprayed film is much higher than that of the HVOF-sprayed film.

4. Discussion

From Figs. 2–4, it was clearly demonstrated that TiO\textsubscript{2} photocatalyst film was successfully deposited on stainless steel substrate by cold spray. Metallic powders can reach a high velocity from 300 to 700 m/s in cold spray\textsuperscript{[13,14]}. TiO\textsubscript{2} powders should reach a higher velocity than metallic powders.
owing to its lower density. When a TiO$_2$ powder impacts on a substrate surface at a high velocity, the spherical powder may deform under high transient impact pressure due to the organic binder agglomerating fine TiO$_2$ particles. The deformation may occur in a way similar to that of metallic powders in cold spray. Therefore, the film was stacked by deformed powder as shown in Fig. 3.

SEM examination shown in Fig. 3 confirmed that the substrate was fully coated with TiO$_2$ film in thickness of 10–15 μm without any bare area. However, it can be seen from Fig. 4 that the diffraction peaks of the substrate were present in the XRD patterns. This fact indicates that the limited thickness of TiO$_2$ film was responsible for the occurrence of XRD peaks of the substrate.

The comparison of the surface morphology shown in Fig. 2c with that of powder (Fig. 2b) suggested that the cold-sprayed TiO$_2$ film has the same stacking microstructure as the powder. From the cross-sectional microstructure shown in Fig. 3, although the film was filled in some epoxy binder to make the sample better, it can be clearly observed that there are some small pores in size of sub-micrometer in the film. These pores resulted from the stacking of the primary particles.

It was also clearly indicated by XRD analysis results of the deposited film that the pure anatase phase as that in the powder is present in cold-sprayed film. During spraying, N$_2$ gas was used as the accelerating gas at a temperature of 300 °C and subsequently, powder particle temperature is lower than 300 °C. Therefore, particle temperature is lower enough to avoid the transformation of anatase phase to rutile phase [15–18]. Consequently, the crystalline structure of the powders is completely retained in the film.

The photodegradation results showed that the photocatalytic degradation of acetaldehyde by TiO$_2$ film is much more active than that by photolysis of UV light. This fact indicated that the cold-sprayed TiO$_2$ film is photocatalytically active. The primary particles was fully retained in the cold-sprayed film, while HVOF-sprayed TiO$_2$ film is composed of small primary particles and some large particles resulting from melted powders [12]. Since large surface area resulting from small particle size does good to photocatalytic activity [12], cold spray is better than HVOF spray in the point view of surface area of the catalyst. The cold-sprayed TiO$_2$ film is in pure anatase phase, while HVOF-sprayed TiO$_2$ coating is composed of both anatase phase and rutile phase [12]. Since the activity of anatase phase is higher than that of rutile phase [12], the cold spray is better than HVOF in the point view of crystalline structure. Therefore, the higher activity of the cold-sprayed film than that of the HVOF-sprayed film is attributed to both larger surface area and higher content of anatase phase.

5. Conclusions

Nanoporous TiO$_2$ photocatalytic film was deposited through cold spray by using agglomerate anatase powder with primary particle size of 200 nm. Results showed that TiO$_2$ film of a mean thickness of 10–15 μm was evenly deposited on the substrate surface. SEM examination revealed that the film presented a rough surface and porous structure. The crystalline structure of the spray powder was completely retained in the film owing to the low temperature of the spray material during the cold spray. It was found that the cold-sprayed TiO$_2$ film was photocatalytically active for photodegradation of acetaldehyde.

Acknowledgements

The project was supported by National Natural Science Foundation of China (Grant No.: 50171052, 50725101).

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