Dominant microstructural feature over photocatalytic activity of high velocity oxy-fuel sprayed TiO₂ coating

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Abstract

TiO₂ photocatalytic coatings were deposited through high velocity oxy-fuel spray using anatase powder and rutile powder as feedstock. The as-sprayed TiO₂ coating was composed of anatase phase and rutile phase. The anatase content in the coating was significantly influenced by fuel gas flow and melting condition of spray powder. A high anatase content of 35% was achieved for the coating deposited using rutile powder. The anatase content in the coating deposited using anatase powder reached 55–65%. The as-sprayed TiO₂ coating was photocatalytically reactive for degradation of acetaldehyde in air. The photocatalytic activity was influenced by spray conditions. The surface morphology and phase structure of coatings deposited at different spray conditions were investigated to clarify the relationship between the coating microstructure and activity. It is found that the photocatalytic activity is significantly influenced by anatase content and surface area.

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1. Introduction

TiO₂ photocatalytic coating attracts much research attention owing to its promising applications to environmental purification, solar cells, sterilization, cancer therapy and antifogging coatings [1–4]. TiO₂ coatings are deposited through many processes such as vapor deposition, sol–gel and thermal spray [2–6]. Among those procedures thermal spray is characterized as a flexible and efficient process which has been widely used to deposit both metallic and nonmetallic coatings.

TiO₂ coatings deposited by conventional flame spray and plasma spray consist of rutile phase and a fraction of anatase phase. The anatase content in the coatings was around 10 to 15% deposited with spray powder at a well melted condition in spite of spray powders crystalline structure [7–8]. Moreover, the anatase content could not be effectively controlled through spray conditions. Photocatalytic degradation results showed that the coatings presented a limited activity. The limited activity was attributed to low anatase content in the coatings, since TiO₂ in anatase phase was superior to rutile phase as a photocatalyst [7–11]. It is reported that the coating with high anatase content could be deposited through high velocity oxy-fuel spray when TiO₂ powder in anatase phase was used as feedstock [12,13]. Our previous study confirmed that a coating having anatase content of about 40% can be deposited even using TiO₂ in rutile structure [14]. Therefore, it can be expected that the as-sprayed TiO₂ coatings present higher photocatalytic activity than conventional plasma sprayed and flame sprayed coatings [12]. However, although high anatase content was obtained through plasma spraying on a polyethylene terephthalates (PET) substrate, the coatings of much different anatase content presented a similar photocatalytic activity [13].

In this paper, TiO₂ coatings were deposited through high velocity oxy-fuel spray using two powders in pure anatase phase and rutile phase as feedstock. Fuel gas at different flow was employed to control the microstructure of the coatings. The influence of spray condition and coating microstructure on the photocatalytic activity was investigated to clarify the dominant microstructural feature over photocatalytic activity of TiO₂ coatings.
2. Experimental

2.1. Materials

Two TiO\textsubscript{2} powders were used as the feedstock for coating deposition. Fig. 1 shows the surface morphologies of two powders. One was anatase powder in a particle size range from 10 to 45 \(\mu\)m. This powder was prepared through agglomerating 0.2 \(\mu\)m ultra-fine particles in pure anatase phase using polyvinyl alcohol as a binder, shown in Fig. 1A. The detailed surface morphology of the powder is shown in Fig. 1B. The other powder shown in Fig. 1C having rutile structure was made by a fuse-crushing process. This powder has a particle size range from 10 to 20 \(\mu\)m. Stainless steel plate was employed as a substrate for coating deposition. Prior to spraying, the substrate was blasted with alumina grits.

2.2. Coating deposition

TiO\textsubscript{2} coatings were deposited with a high velocity oxy-fuel (HVOF) system (CH-2000, Xi’an Jiaotong University), and the detailed description of this system can be found elsewhere [15–16]. Propane was used as a fuel gas. During spraying, the flow of propane was altered to control the heating condition of spray powders. The flow of oxygen was fixed at 402 l/min. Nitrogen was used as powder carrier gas. Stand-off distance was maintained at 130 mm. The spray gun was manipulated by a robot (Motoman) and traversed at a relative speed of 500 mm/s over the substrate.

2.3. Characterization of TiO\textsubscript{2} coating

The crystalline structure of TiO\textsubscript{2} coating was characterized using X-ray diffraction (XRD) (Rigaku D/max-2400) by Cu K\(\alpha_1\) radiation. The operating condition was 40 kV and 100 mA. The goniometer was set at a scan speed of 5\(^\circ\)/min for 2\(\theta\). The anatase content in TiO\textsubscript{2} coating was estimated based on the relative peak area of anatase (101) and rutile (110) peaks in XRD pattern [17].

The topographic morphology of the coatings was examined by scanning electron microscopy (SEM) (Hitachi S2700).

The photocatalytic performance of TiO\textsubscript{2} coatings was evaluated through photodegradation of acetaldehyde under the UV illumination with a dominant wavelength of 254 nm. An experimental setup shown in Fig. 2 was assembled to carry out the photodegradation. A 110 ml quartz cuvette was used as a photocatalytic reactor. The UV light intensity at coating surface...
was about 1 mW/cm². The acetaldehyde concentration in the reactor was determined by gas chromatography (GC) (Agilent 6890). The photocatalytic activity was estimated through fitting the change of the relative concentration of acetaldehyde with UV-irradiation time following Langmuir–Hinshelwood principle [11].

3. Results

3.1. Effect of fuel gas flow on the coating phase structure

XRD patterns of the as-sprayed TiO₂ coating showed that all coatings were composed of anatase phase and rutile phase in spite of the origin powder structure. Furthermore, both the anatase phase and rutile phase in the coating showed no evidently preferential orientation, whereas the preferential orientation often occurred in the coatings fabricated through conventional flame spray and plasma spray [7,8,18].

Fig. 3 shows the effect of fuel gas flow on the anatase content in the coatings deposited using two powders. On the one hand, as rutile powder was used as feedstock, the anatase content was 10% at the fuel gas flows of 24 and 30 l/min. The content of anatase phase increased with the increase of fuel gas flow. A maximum anatase content of 35% was obtained under a fuel gas flow of 48 l/min. On the other hand, as anatase powder was used as feedstock, 60% anatase content was obtained at fuel gas flow from 24 to 30 l/min. The anatase content decreased to about 30% with the increase of fuel gas flow from 30 to 42 l/min. When the fuel gas flow was increased further to 48 l/min from 42 l/min, the anatase content of the coating was increased again to 35%.

3.2. Effect of fuel gas flow on the coating microstructure

Fig. 4 shows surface morphologies of the TiO₂ coatings deposited using the anatase powder at different fuel gas flows. A lot of ultra-fine particles were present in the coating, which was clearly observed from Fig. 4A. The particle size of these ultra-fine particles was the same as that of starting powder as shown in Fig. 1B. In the coating deposited at fuel gas flow of 36 l/min, most particles had sizes ranging from 0.5 to 2 μm. It can be found that the coating consisted of large particles with sizes from 1 to 3 μm when the fuel gas flow was 48 l/min.

Fig. 5 shows surface morphologies of the TiO₂ coatings deposited using rutile powder at different fuel gas flow. The splats with a relative smooth surface morphology were formed at fuel gas flow of 24 l/min. The splats in the coatings deposited at fuel gas flows of 36 and 48 l/min presented a much rougher topographic morphology.
3.3. Effect of fuel gas flow on the photocatalytic activity

Fig. 6 shows the change of relative concentration of acetaldehyde with radiation time by using TiO$_2$ coatings HVOF sprayed using two powders at different fuel gas flow. The result for blank reaction is shown in Fig. 6A for comparison. When there was no coating in the reactor, acetaldehyde concentration decreased with the reaction time due to the directly photolysis of acetaldehyde by 254 nm UV illumination. 40% of the acetaldehyde was decomposed by photolysis in 130 min. When the as-sprayed coating was put in the reactor, the acetaldehyde concentration decreased faster than that for blank reaction. This result indicates that the photocatalytic degradation of acetaldehyde was much more significant than the photolysis.

Fig. 7 shows the effect of fuel gas flow on photocatalytic activity of HVOF sprayed coatings using two powders. For the
coatings deposited using rutile powder, its photocatalytic activity increased a little with the increase of fuel gas flow. However, the photocatalytic activity of the coatings deposited using anatase powder decreased significantly with the increase of fuel gas flow. When the fuel gas flow was lower than 30 l/min, the coatings deposited using anatase powder presented the highest photocatalytic activity of $2.5 \times 10^{-2} \text{min}$, which was two times higher than the other coatings.

4. Discussion

Two major phases of TiO$_2$ photocatalyst are anatase and rutile. Rutile is one of the stable crystalline polymorphs of titania but anatase is one of the low-temperature metastable polymorphs. Anatase phase transforms to rutile under annealing treatment at a high temperature [11]. The phase transformation at solid state from anatase to rutile may not spontaneously take place at ambient condition [14]. In HVOF spraying, TiO$_2$ particles are heated to a fully molten or partially molten state before impacting on a substrate, which depends on flame condition. After particles impact on a substrate, the liquid fraction of droplet spreads to a splat and solidifies under a high cooling rate over $10^6 \sim 10^8 \text{K/s}$ [19]. Under such splat cooling condition, metastable phase, such as $\gamma$-Al$_2$O$_3$ in HVOF alumina, is easily formed in the coating [20]. Therefore, anatase phase was easily formed from the rapid cooling of the TiO$_2$ splat.

SEM results showed that the TiO$_2$ coatings deposited using rutile powder were in typical splat stacking structure. This fact means that spray powders were in a good melting condition. The XRD results clearly showed that anatase phase was formed in TiO$_2$ coating deposited with rutile powder. For coating deposited using rutile powder, the anatase content of 35% is much higher than that in conventional flame sprayed or plasma sprayed TiO$_2$ coatings. The anatase phase forming in the coating results from rapid splat cooling during HVOF spraying [14].

It is clearly seen that much different surface morphology is observed for TiO$_2$ coatings deposited using anatase powder. Since propane was used as fuel gas for combustion in this study, the increase of propane flow increases the flame temperature. Increasing propane flow from 24 to 48 l/min means almost doubled flame power under the condition of complete combustion. As a result, both the flame temperature and length of the flame are increased. Both effects enhance the heating of flame to powder, resulting in increase of melted fraction in individual particles. The coatings have particle stacking structure. The small particles in the coating deposited at a fuel gas flow of 24 l/min have the same size as the primary particle size in the spray powder. This suggests that the anatase powder was not well melted under these spray conditions.

The estimation based on XRD analysis showed that the coatings deposited at fuel gas flow of 42–48 l/min presented the anatase content of 25–35%, and at fuel gas flow of 24–30 l/min the coatings contained much more anatase of 55–65%. Such high anatase content in the coatings deposited at low fuel gas flow is due to the fact that a fraction of anatase phase in the starting spray powder was retained in the coating. However, when the deposition was carried out at a high fuel gas flow using the powders in both anatase crystalline and rutile crystalline, both the anatase content and particle size in the coating became comparable.

It is revealed that if spray powder is in a good melting condition, the coatings will present a similar microstructure in spite of the starting powders structure. For conventional plasma spray and flame spray, spray powder often reach a good melting condition. As a result, those coatings contain a limited anatase content.

Fig. 8 shows the relationship between photocatalytic activity and anatase content in TiO$_2$ coatings deposited using two powder. A data using pure rutile coating, which was obtained by annealing treatment at a high temperature, was also shown for comparison. It can be found that the photocatalytic activity of thermally sprayed TiO$_2$ coatings increases with the increase of anatase content in the coating. However, as clearly shown by Fig. 8, the relation between photocatalytic activity and anatase content is not linear. This result indicates that the photocatalytic activity of TiO$_2$ coating is also influenced by surface area.

Among all coatings, the coatings deposited using anatase powder at low fuel gas flow showed the highest photocatalytic activity. It should be attributed to two structural aspects. One is that those coatings contain the highest anatase content, since anatase phase is more reactive than rutile phase as a photocatalyst. The other is that those coatings are of the largest surface area, since it is composed of very small primary particles in the diameter of 0.2 $\mu$m. This is consistent with the experiment reported by Fukumoto et al. [12].

It is also found that the coating deposited using rutile powder at fuel gas flow of 36 l/min shows a relative low activity, although it presents a high anatase content of 50%. On the one hand, in these coating, the outer thin layer of small particles near to the coating surface may transform to rutile phase from anatase phase due to the high fuel gas flow and therefore high flame temperature. However, the outer part is much more important than the sub-surface part of the coating. On the other hand, the surface area is smaller than that of the coating deposited at lower fuel gas flow. It suggested that the photocatalytic activity is also influenced by the phase distribution within the coatings.
5. Conclusions

High velocity oxy-fuel spray was employed to deposit TiO$_2$ photocatalytic coatings using anatase powder and rutile powder as feedstock. The as-sprayed TiO$_2$ coating was composed of anatase phase and rutile phase. The anatase content in the coating was significantly influenced by fuel gas flow and melting condition of spray powder. A high anatase content of 35% in the coating deposited with rutile powder was achieved. The anatase content in the coating deposited using anatase powder reached 55–65%. This high anatase content is contributed by the retention of the anatase in the starting powder. The as-sprayed TiO$_2$ coating was photocatalytically reactive for degradation of acetaldehyde in air. The high activity of the coatings deposited at low fuel gas flow using anatase powder is attributed to high anatase content and large surface area.

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