Microstructure and photocatalytic performance of high velocity oxy-fuel sprayed TiO₂ coatings

Guan-Jun Yang¹, Chang-Jiu Li¹,a,*, Feng Han¹, Akira Ohmori¹

¹State Key Laboratory for Mechanical Behavior of Materials, Welding Research Institute, School of Materials Science and Engineering, Xi’an Jiaotong University, Xi’an, Shaanxi 710049, PR China

bJoining and Welding Research Institute, Osaka University, 11-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan

Received 12 July 2003; received in revised form 13 January 2004; accepted 6 February 2004

Available online 12 April 2004

Abstract

Titanium dioxide photocatalytic coatings were deposited through high velocity oxy-fuel (HVOF) spraying agglomerate anatase powder. Different spray parameters (e.g. flow of fuel gas) were utilized with the aim to reveal their influence on microstructure and photocatalytic performance of the HVOF titania coatings. The microstructure of the coatings was characterized using X-ray diffraction and scanning electron microscope. The photocatalytic performance of the coatings was evaluated through analyzing photocatalytical degradation of phenol using an ultraviolet spectrometry. Results showed that the phase compositions of the titania coatings were significantly influenced by melting state of the sprayed particles, which was influenced mainly by fuel gas flow. The HVOF TiO₂ coating with up to 70% anatase phase can be obtained through assuring a limited melting state of the titania powder during the coating deposition. A content of 40% of the anatase phase was obtained in the coating deposited from well-melted particles. Furthermore, the present HVOF titania coatings showed promising effect in photocatalytically degrading phenol in the solution. It was found that the complete mineralization of phenol was controlled by the degradation of the intermediates resulting from the decomposition of phenol. It was also noted that the presence of certain rutile phase in the HVOF titania coatings enhanced their photocatalytic performance.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Titanium oxide; Phase transitions; Photocatalysis; High velocity oxy-fuel

1. Introduction

Wastewater treatment and purification of polluted air have attracted extensive attentions in the last decades. Photocatalytic degradation of harmful and toxic organic pollutants, using semiconductors, such as TiO₂, ZnO, Fe₂O₃, CdS, ZnS, is one of the effective ways [1,2]. Among those semiconductors, titanium dioxide is the most promising photocatalyst owing to its excellent photocatalytic activity, physical and chemical stabilities, and non-toxicity. Titania coatings in the immobilized form are more desirable and competitive than titania powders for their application in such field.

Thermal spray process has been widely used to deposit coatings, including photocatalyst coatings [3–7]. During thermal spraying, powders are heated and accelerated and then projected onto a substrate, followed by flattening, rapid cooling and solidification processes, which results in a typical quenched microstructure. The investigation on TiO₂ coatings deposited through conventional flame spraying and plasma spraying showed that the coatings consisted mainly of rutile phase with only a low fraction of anatase phase, despite the crystalline structure of the initial powders [3,4]. However, the photocatalytic performance is significantly influenced by the crystalline structure of TiO₂. The performance of TiO₂ in anatase phase is more effective than that in rutile phase [8,9]. Therefore, it is significantly important to minimize the transformation from anatase to rutile during the spraying. A study on microstructure of thermally sprayed TiO₂ coatings and its effect on the photocatalytic performance are necessary for the development of the excellent TiO₂ photocatalyst.

In the present study, high velocity oxy-fuel (HVOF) process was employed to deposit TiO₂ coatings. The
effects of spray conditions on the microstructure and the photocatalytic performance of the titania coatings were investigated.

2. Experimental

2.1. Materials

TiO$_2$ powder with pure anatase crystalline structure was used as the feedstock. The starting anatase powder (−45+10 µm) was prepared through agglomerating 0.2 µm ultra-fine particles using polyvinyl alcohol as the binder. Stainless steel plate sample with dimensions of 105 × 25 × 1.5 mm was employed as a substrate for coating deposition. Prior to spraying, the substrate was blasted with 24 mesh alumina grits.

2.2. HVOF spraying

A home-developed HVOF system (CH-2000, Xi’an Jiaotong University) was used for the coating deposition. The system has been described in detail elsewhere [1]. Propane was used as the fuel gas. The pressure of propane was set at 0.4 MPa during coating deposition. The pressure and flow of oxygen were set at 0.55 MPa and 402 l/min, respectively. Nitrogen was used at a pressure of 0.4 MPa as the powder carrier gas. The spray distance from the nozzle exit to the substrate was 130 mm. During spraying, the flow of propane was altered to modify melting state of the spray powders.

2.3. Characterization of sprayed coating

Topographical morphology of the sprayed coatings was examined using scanning electron microscope (SEM, JSM5800). The crystalline structure was characterized by X-ray diffraction analyzer (XRD, Rigaku D/max-2400) using Cu K$_\alpha$ radiation. The operating conditions were 40 kV and 100 mA. The goniometer was set at a scan rate of 5°/min for

3. Results and discussion

3.1. Microstructure of the titania coating

XRD analysis showed that the HVOF TiO$_2$ coatings deposited by anatase powder consisted of both anatase and rutile phases. Fig. 2 shows the effect of fuel gas flow on the anatase content in the coatings. It was noted that the anatase content in the coatings decreased from 70 to 30% with the change of the fuel gas flow. As the fuel gas flow was less than 36 l/min, the resultant coating contained more than 55% anatase phase. This is considerably higher than those reported for plasma-sprayed TiO$_2$ coatings [3,4]. It is also evident that the anatase content in HVOF TiO$_2$ coatings decreased as the flow of propane increased from 30 to 42 l/min. The anatase content increased with a further increase in fuel gas flow.

Fig. 3 shows the surface morphology of the HVOF TiO$_2$ coating deposited with a fuel gas flow of 24 l/min. It can be

Fig. 1. Schematic diagram of experimental setup for the photocatalytic degradation of phenol.

Fig. 2. Effect of fuel gas flow on the anatase content in the HVOF sprayed coating.

20. The anatase content in the coatings was estimated based on the following equation:

$$C_A = \frac{A_A}{A_A + A_R} \times 100\%$$

where $C_A$ is the anatase content, $A_A$ and $A_R$ are the integrated area intensity of the (110) peak for rutile and that of the (101) peak for anatase, respectively.
seen that the surface morphology of the sprayed coating was similar to that of the starting powder. The particles presented the same size of 0.2 μm as that of ultra-fine particles in the starting powder. This fact suggests that much limited melting occurred for the in-flight particles. Accordingly, it can be considered that the high anatase content in the coating under such spray conditions was mainly attributed to the partially melted particles, which contributed to the remaining of their original crystalline structure after the spraying.

It can be found from the results reported [11,12] that, as HVOF process was operated under given oxygen pressure and flow, the flame temperature will be increased with the increase in fuel gas flow under the present conditions. The increase in the flow of fuel gas enhanced the heating of the particles. Consequently, melting state of the spray particles was improved. Fig. 4a, b show the surface morphologies of the titania coatings deposited with the fuel gas flows of 36 l/min and 48 l/min, respectively. It shows that from the surface morphology, many particles with a size of 0.5 to 2 μm, which were larger than those in Fig. 3, adhered on the surface of the coating deposited at a fuel gas flow of 36 l/min. This corresponded to an improved melting state of the particles. As the fuel gas flow was 48 l/min, the surface morphology of the coating (Fig. 4b) revealed that the coating was composed mainly of substantially melted particles. Despite sufficient melting state at a fuel gas flow of 48 l/min, the TiO₂ coating containing 40% anatase phase was deposited. This anatase content was higher than that in the coatings deposited at a fuel gas flow of 42 l/min. Compared with the low anatase content in the plasma-sprayed titania coatings [3,4], the present study suggests that the TiO₂ coating containing a high anatase content can be deposited using HVOF process. Also, the undesirable effect of the well melting state of the titania particles on the phase transformation from anatase to rutile can be minimized during the HVOF spray.

Among three crystalline structures of TiO₂, rutile phase is the thermally stabllest, while the other two phases, anatase and brookite, transform to rutile at temperatures from 450 to 950 °C, depending on the titania preparation process [13–15]. Under HVOF spray conditions, the flame can reach a velocity over 1500 m/s [10,16]. Accordingly, spray particles can be accelerated to a much higher velocity in HVOF spraying process than in the conventional plasma spraying process. Compared with the velocity less than 300 m/s attained by the particles during plasma spraying [17], a high particle velocity from 600 to 1000 m/s can be achieved within HVOF flame [16]. As a molten particle at a higher velocity impacts on a substrate surface, high kinetic energy drives the particle to flatten, and finally to form a thinner splat. For the titania coating, the rapid cooling and solidification of the thin splat [18] may result in the formation of highly quasi-stable anatase phase.

3.2. Photocatalytic performance of the titania coating

Fig. 5 shows the UV spectra of the phenol solutions after photocatalytic degradation with different times. This HVOF titania coating was deposited at a propane flow of 36 l/min. For comparison, the spectrum of the initial solution before photocatalytic degradation was also shown in Fig. 5, as indicated by the curve with 0 min. Phenol shows an absorption band at the wavelength of 269 nm. After photocatalytic degradation, the characteristic absorption peak of phenol gradually decreased with degrading time. The concentration of phenol in the solution was quantitatively estimated using this characteristic peak of the spectrum. It can be clearly found from Fig. 6 that the phenol concentration in the solution decreased with the degrading time. It can
be degraded to a relative concentration of 10% in 60 min. For comparison, the change of the phenol concentration in the solution irradiated only by ultraviolet light without the TiO₂ coating was also given in Fig. 6. It is clear that the HVOF titania coating is effective in photocatalytically degrading phenol.

However, it is noticed that beyond wavelength of 225 nm, the spectra showed an increased intensity with the increase in degrading time till 25 min. Moreover, it is evident that several small humps were present on the spectrum. This implies that the photocatalytic degradation of phenol resulted in the formation of other intermediates such as hydroquinone, catechol and p-benzoquinone. With further degradation, the spectrum descended gradually to a low level, which implies that those benzene series of organic intermediates decomposed to organic acids. Those results clearly indicated that the phenol can be photocatalytically and completely degraded by the present HVOF TiO₂ coatings, although the degradation of the intermediates takes a certain long time compared with initial degradation of phenol.

From the results shown in Fig. 6, it is also evident that the HVOF TiO₂ coatings deposited at a higher flow of fuel gas were more effective for the degradation of phenol than those deposited at a lower flow. Taking into account the crystalline structure of the HVOF TiO₂ coatings (Fig. 2), it suggests that the HVOF TiO₂ coating containing certain rutile crystalline phase provides a better photocatalytic performance. It is generally believed that TiO₂ in anatase crystalline form is more effective as a photocatalyst [8,9]. It was also reported that anatase phase with a small amount of rutile phase addition was more effective than mono-anatase phase [19,20]. Compared with the results reported [8,9,19,20], the present results showed a quite different dependency of photocatalytic performance on the crystalline structure of TiO₂. Such results may be associated with the microstructural features of TiO₂ deposited by thermal spray process. Nevertheless, a detailed investigation is still necessary to clarify the detailed phases in the HVOF TiO₂ deposit, and hence to further improve the photocatalytic performance of the coatings.

4. Conclusions

HVOF titania coatings were deposited using agglomerate anatase powder. The coatings were composed of both anatase and rutile phases. The anatase content in the coatings altered from 30 to 70% depending on the flow of fuel gas. The phase composition of the coatings was significantly influenced by fuel gas flow. The high fuel gas flow led to the improvement of melting state of the sprayed particles. The high anatase content (> 60%) in the coating deposited using low fuel gas flow resulted from the retention of the original structure of the powders due to their limited melting state. However, the TiO₂ coating containing approximately 40% anatase was made from well-melted TiO₂ particles.

Phenol in the solution can be photocatalytically and rapidly degraded through the HVOF TiO₂ coatings. The complete mineralization of phenol seemed to be mainly controlled by the degradation of the intermediates resulting from decomposition of phenol. The present results showed that the HVOF TiO₂ coating containing certain rutile phase presents a better photocatalytic performance.

Acknowledgements

The present project is supported by National Natural Science Foundation of China (Grant No.: 50071044), the Education Promotion Project of Xi’an Jiaotong University and Natural Science Foundation of Xi’an Jiaotong University. Authors would like to thank Dr Hua Li of Nanyang Technical University and Dr Y. He of Canada Customs and Revenue Agency for their kind revision of the manuscript.
References