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The Formation Behavior of TiO_2 Thermal Sprayed Coatings Using Nano-Powders and Their Photo-Catalytic Properties†

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Abstract

TiO_2 coatings were prepared by High Velocity Oxy-Fuel (HVOF) spraying using agglomerated sub-micron and nano-TiO_2 powders (200nm, 30nm, 7nm). The effects of various spraying conditions on microstructure, anatase phase ratio, coating thickness have been investigated and then photo-catalytic properties were evaluated. It was found that anatase phase ratio decreased drastically with increasing fuel gas pressure in the case of 7nm agglomerated powders (P_7 powders), while a higher anatase ratio was obtained in the case of agglomerated 200nm and 30nm powders (P_{200} and P_{30} powders). Anatase ratios greater than 60% could be achieved when agglomerated 30nm powders were sprayed. This means that 30nm agglomerated powders were showing lower susceptibility to heat effect and provided higher photo-catalytic activity. When agglomerated 7nm agglomerated powders were sprayed, individual particles were easily subjected to heat affect and then became 30nm by rapid grain growth. On the other hand, since large increases of anatase particle (grain) size were not detected when agglomerated 30nm powders were sprayed, it was assumed that an approximately 30nm particle was the limit size and optimum size for HVOF spraying.

These coatings showed photo-catalytic decomposition of gaseous acetaldehyde (CH_3CHO). As a result of photo-catalytic experiments, TiO_2 coating formed by HVOF spraying using 30nm powder showed a higher decomposition rate because of higher anatase ratio.

KEY WORDS: (Nano), (Agglomerated powder), (TiO_2), (HVOF spraying), (Anatase)

1. Introduction

TiO_2 is widely used as a photo-catalytic materials for decomposition of polluted water and harmful chemical compounds [1)-5)]. Powders with a large specific surface are promising to fully utilize this photo-catalytic property. However, in many case, the powers have to be fixed on the targeted substrate for practical applications. Although there have been many reports [6)-7)] about the preparation of thin film TiO_2 coatings, such as sol-gel processes, there are few techniques that can deposit thick coatings. The high velocity oxy-fuel (HVOF) is a typical example of this technique, thermal sprayed coatings can produce thick layers with many porous structure in short times. These pores are very useful sites for photo-catalytic reaction. In addition, thermal sprayed coatings can be easily prepared on many materials such as plastics, metal and ceramics.

It is anticipated that if nano-powders could be deposited, the fixed TiO_2 coating could show photo-catalytic activity. However, none of their spray conditions have been specified for achieving nano-TiO_2 coatings. Thus, one of the major objectives of this study is to investigate the basic behavior of the TiO_2 coating. It is known that easy phase transformation to rutile phase occurs above the 1188K [8)], however, retaining anatase phase is essential to achieve high photo-catalytic activity. In this research, the effect of agglomerated TiO_2 powders with sub-micron and nano-size primary particles on the microstructure and crystal structure were investigated using High Velocity Oxy-Fuel (HVOF) spraying and then their photo-catalytic activities were evaluated.

2. Experimental

A Cu undercoat was previously sprayed to increase adhesion strength between topcoats (TiO_2) and substrates. **Fig. 1** shows the surface morphology of anatase TiO_2 powders with an average size of 33.7 μm. Polyvinyl alcohol was used as a binder and feedstock powders were

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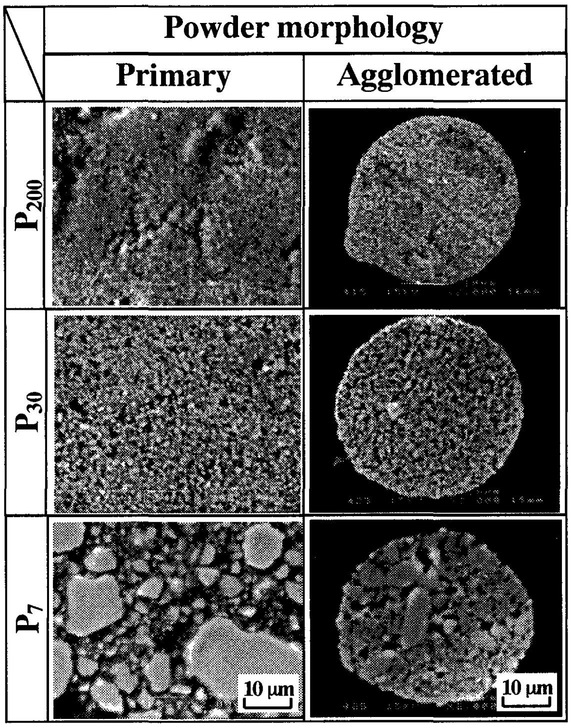

Fig. 1 Surface morphologies of primary and agglomerated TiO_2 powders.

Table 1 Spraying conditions of HVOF.

Fuel gas : 70% C_2H_2 + 30% C_3H_6

O_2 pressure (MPa) (Flow rate (l/min))	**0.55** (300)
Fuel gas pressure (MPa)(Flow rate (l/min))	**0.20~0.45**(31~71)
Carrier gas pressure (MPa)	**0.10**
Spraying distance (mm)	**70**
Spraying atmosphere	**Air**
Traverse speed of gun (m/s)	**1.7×10^{-1}**

synthesized from 200nm, 30nm and 7nm particles. X-ray diffraction was employed to detect anatase and rutile phases with Cu K_α radiation. Anatase phase ratio was calculated [9)] and then grain size was also estimated and by using the Sherrer formula.

In this research, τ (ks) was used as decomposition time to evaluate photo-catalytic activity of TiO_2 coatings and τ value was defined as time when the concentration of gaseous acetaldehyde (CH_3CHO) becomes C_0/e [10)] (C_0 : primary concentration of CH_3CHO before irradiation , e: a natural logarithm, C_0/e means that C_0 divided by e). The lower . value means higher photo-catalytic activity and higher decomposition rate of gaseous acetaldehyde.

The spraying was carried out by HVOF apparatus. **Table 1** show HVOF spraying conditions. The fuel gas used was a mixture (70%C_2H_2+30%C_3H_6) and the powder carrier gas was nitrogen. The fuel gas pressure has been changed from 0.20 to 0.45MPa in the present study. SUS304 plate substrates were used for thermal spraying.

3. Results and Discussion

P_{200}, P_{30} and P_7 agglomerated powders were sprayed. **Fig. 2** shows the effect of fuel gas pressure on anatase ratio of TiO_2 coatings. The fine 7nm powders have the highest susceptibility to heat and therefore, it is apparent that the 7nm anatase particle is easily transformed into the rutile phase during thermal spraying. In the case of P_7 powders, the anatase ratio changed from 86% to 5% with increasing fuel gas pressure and exhibited highly dependency on thermal spray condition (especially, fuel gas pressure). It should be noted that an anatase ratio more than 50% could be obtained when relatively lower fuel gas pressure was used. Although it is well reported that the transformation to rutile phase easily occurs above 1188K, it is suggested that the transformation temperature for fine 7nm particles becomes drastically lower.

Although the large alternation of anatase ratio against gas pressure was not recognized as compared to P_7 powder, the similar tendency was also observed in the case of P_{30} and P_{200} powders. The anatase ratio was always kept higher (more than 50%) and HVOF spraying using P_{30} powders could provide more than 100μm thicknesses as shown in **Fig. 3**.

This higher ratio achieved thickest coatings in all experiments. On the other hand, the average coating thickness became 10μm for P_{200} coatings and it was difficult to obtain thick coatings although P_{200} powders have the lowest susceptibility to heat and more than 70% anatase ratio was detected. According to X-ray diffraction patterns, the high peak of the Cu undercoat was detected since a uniform thickness of TiO_2 deposition could not be obtained. Thick TiO_2 coatings are suitable for use as photo-catalytic applications for long-term periods, particularly, when sprayed photo-catalytic coatings are used around natural environments.

Fig. 4 shows anatase particle (grain) size of TiO_2 coatings. The thermal effect on nano-powders was investigated by measuring this particle size from X-ray diffraction patterns. Prior to thermal spraying, the anatase particle size of as-agglomerated powders were measured. This measured values are also shown in Fig. 4. The anatase particle size of P_{200} coating changed little with increasing fuel gas pressure, the large increases were also not detected when P_{30} powders were sprayed. When P30 and P_7 coatings were compared, the anatase particle size became approximately the same after spraying. It was found that the individual 7nm powders grew by thermal effects during HVOF spraying. However, individual 7nm anatase particles were not transformed into 7nm rutile particles, and it was found that transformation into the rutile phase occurred with thermal growing. Since many agglomerated 7nm powders became 30nm particle size coatings after spraying, it is assumed that the 30nm TiO_2 particle is the critical size when nano-size powders are sprayed by HVOF. These sprayed nano-coatings should show large specific surface areas, therefore, it is necessary to investigate whether the application to photo-catalytic activity is possible or not. Because

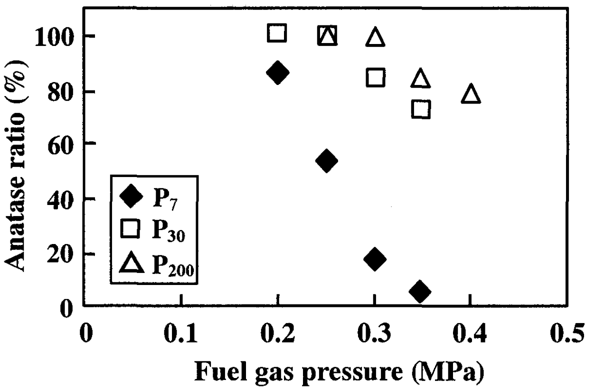

Fig. 2 Anatase ratio of TiO_2 coatings formed by various fuel gas pressure.

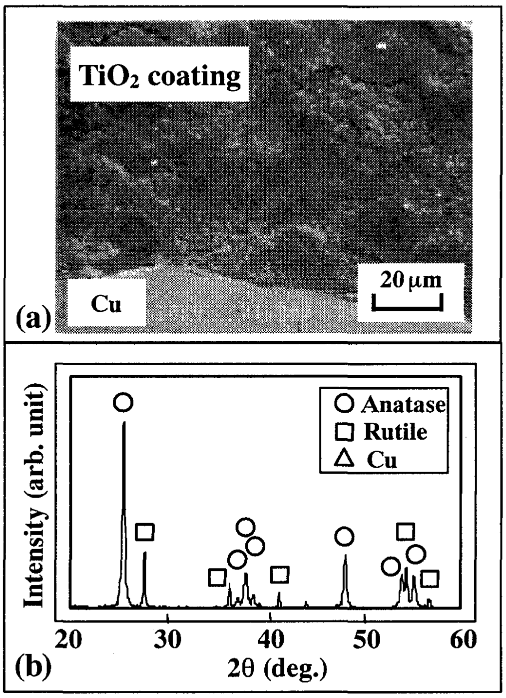

Fig. 3 The cross sectional image (a) and X-ray diffraction pattern (b) of TiO_2 coatings [Fuel gas pressure : 0.35MPa].

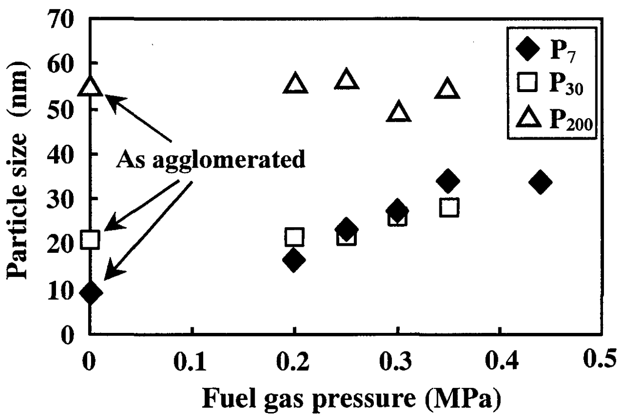

Fig. 4 Anatase particle (grain) size of TiO_2 coatings formed by various fuel gas pressure.

gaseous acetaldehyde is major representative of the bad smell component of smoking cigarettes, the photo-catalytic property was evaluated by using gaseous acetaldehyde.

Fig. 5 shows the photo-decomposition characteristic of gaseous acetaldehyde. It was clear that anatase phase ratio had a large influence on photo-catalytic decomposition. As expected, TiO_2 coatings which showed higher anatase ratio exhibited higher photo-catalytic activity (lower τ value) for every coating. Since the large alternation of anatase ratio was recognized in the P_7 coatings, the τ value was also drastically changed. It has been anticipated that 7nm-powders with a large specific surface promised to fully utilize the photo-catalytic property, however, the measured activity was not the highest in the all sprayed coatings. Although P_7 coatings with higher anatase ratio showed higher decomposition rates of acetaldehyde, the photo-catalytic reaction sites on the surface may decrease because of thermal growing to the 30nm size occured during HVOF spraying.

Of all the sprayed TiO_2 coatings, the all P_{30} coatings always showed higher activity (approximately anatase 100%), the lowest τ value that could be measured. It means that 100ppm gaseous acetaldehyde was decomposed to less than 5ppm after 1.8ks. In the range of 70~100% anatase ratio of P_{30} and P_7 coatings, the large differences are not recognized.

Since transformation to rutile phase easily occurs in the P_7 coatings and highly depends on fuel gas pressure, in terms of anatase phase stability and photo-catalytic activity, HVOF spraying using 30nm-agglomerated powders could be recommended.

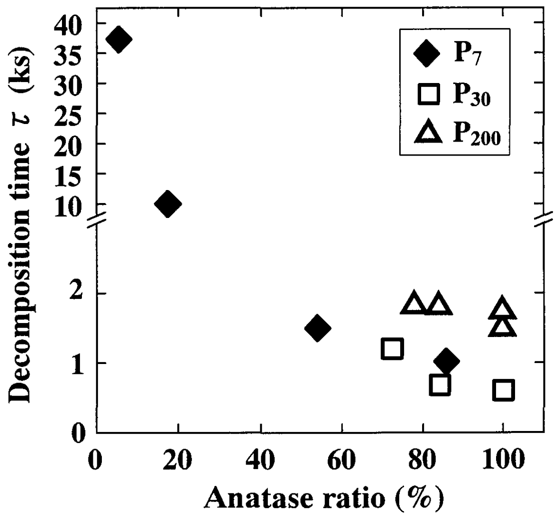

Fig. 5 Relationship between photo-catalytic properties and anatase ratio.

4. Conclusions

Three types of sub-micron and nano-size agglomerated TiO_2 powders were sprayed and then both the basic behavior and photo-catalytic activity were investigated.

(1) When P_7 powders were sprayed, the anatase ratio of TiO_2 coatings changed from 86% to 5% with increasing fuel gas pressure, and, it should be noted that an anatase ratio more than 50% could be obtained when relatively lower fuel gas pressure was used. On the other hand, a large decrease of anatase ratio was not detected and kept a higher level (more than 50%) when P_{30} powders were sprayed.

(2) It was found that the individual 7nm powders grew during HVOF spraying and the transformation into rutile phase occurred simultaneously. Since many agglomerated 7nm powders became 30nm anatase particle (grain) size after spraying, it is assumed that 30nm TiO_2 particle was a limit size and optimum size when nano-size powders were sprayed by HVOF.

(3) All P_{30} coatings showed higher activity and both P_7 coatings contained higher anatase ratios and the P_{30} coating showed similar photo-catalytic decomposition rates of gaseous acetaldehyde since the 7nm particles became 30nm particle size by HVOF spraying.

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