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Cold Spraying of TiO_2 Photocatalyst Coating With Nitrogen Process Gas

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Titanium dioxide (TiO_2) is a promising material for photocatalyst coatings. However, it is difficult to fabricate a TiO_2 coating with anatase phase by conventional thermal spray processes due to a thermal transformation to rutile phase. In this paper, anatase TiO_2 coatings were fabricated by the cold spray process. To understand the influence of process gas conditions on the fabrication of the coatings, the gas nature (helium or nitrogen) and the gas temperature are investigated. It was possible to fabricate TiO_2 coatings with an anatase phase in all spraying conditions. The process gas used is not an important factor to fabricate TiO_2 coatings. The thickness of the coatings increased with the process gas temperature increasing. It indicates that the deposition efficiency of the sprayed particles can be enhanced by controlling the spray conditions. The photocatalytic activity of the coatings is similar or better than the feedstock powder due to the formation of a large reaction area. Concludingly, cold spraying is an ideal process for the fabrication of a TiO_2 photocatalyst coating.

Keywords ceramic, cold spray, deposition, nitrogen oxide, process gas

1. Introduction

Titanium dioxide (TiO_2) is an attractive material with respect to its photocatalytic property. To use a TiO_2 photocatalyst coating to remove air pollutants such as nitrogen oxide (NO_X) and acetaldehyde, formation of a large area coating is required. Conventionally, thermal spray processes have been widely used for the fabrication of a thick and large area coating. Therefore, there are a number of studies about fabrication of a TiO_2 photocatalyst coating by several thermal spray processes (Ref 1-5). Fabrication of a TiO_2 coating is not difficult by thermal spray processes, though it has been difficult to obtain a coating which has a high photocatalytic property. The photocatalytic performance of TiO_2 is significantly affected by its crystal structure. TiO_2 in anatase phase provides a higher photocatalytic activity than that in rutile phase (Ref 6, 7). The anatase phase irreversibly transforms into rutile phase over 900 °C which is lower than the melting temperature of TiO_2 (1908 °C). Since with processes having a temperature higher than the melting temperature of TiO_2, thermal-sprayed coating is formed by the deposition of molten or semi-molten droplets, it means that the phase transformation of TiO_2 can not be avoided in conventional thermal spray processes.

Cold spraying has been developed as a new technology to obtain high-quality coatings due to its lower heating of the feedstock powder materials (Ref 8-10). Ductile materials such as copper and aluminum have been effectively sprayed by this process and superior coating properties in thermal and electrical conductivity compared with conventional thermal-sprayed coatings have been indicated (Ref 8). In this process, small (1-50 μm) particles are accelerated by a supersonic gas stream at a temperature that is lower than the melting temperature of the material, resulting in coating formation from particles in the solid state. As a consequence, a deposited coating can avoid any high-temperature oxidation, evaporation, phase transformation, thermal stress, and other common problems encountered in traditional thermal spray processes. Cold spraying seems to be a suitable process for the fabrication of a photocatalyst TiO_2 coating with an anatase phase. However, there are few reports about the fabrication of a ceramic coating by cold spray (Ref 11-14). It is due to the deposition mechanism of the cold-sprayed particles. The cold-sprayed particles are adhered to the substrate surface by the plastic deformation of the particle itself. The plastic deformation and the adhesion can be occurred when the particle velocity is higher than a critical velocity in cold spray process (Ref 15). Therefore, the spray materials have been limited as ductile metals or their composites. In other words, brittle materials such as ceramics have been considered to be difficult to deposit by cold spray process.

The possibility to fabricate a TiO_2-thick coating by cold spray is shown in previous studies (Ref 16, 17). However, the coatings were fabricated with limited spray conditions using helium (He) as process gas. He is useful in the cold

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spray process. Because He can accelerate the sprayed particles faster than using nitrogen (N_2) due to lower molecular weight (Ref 18). However, it is not suitable for industrial use due to its high price compared with N_2. In this paper, TiO_2 coatings were fabricated using He and N_2 as the process gas in order to investigate the influence of the process gas nature. Furthermore, the process gas temperature was also changed in order to investigate its influence on the sprayed coating properties. These gas conditions (nature and temperature) are well known as important factors of the cold spray process for the fabrication of a metal coating. The photocatalytic property of the coatings fabricated is also investigated in this study.

2. Experimental Procedure

All experiments were carried out with a self-designed cold spray apparatus. A schematic image of the cold spray apparatus is shown in Fig. 1. The de Laval spray nozzle was designed by numerical simulation (CFD2000: CAE Solutions, Tokyo, Japan). The typical spray parameters used are listed in Table 1. The spray parameters such as gas pressure were optimized by spraying of copper. The gas temperature and pressure were measured by the sensors placed at the mixer. TiO_2 powder (TAYCA, Okayama, Japan) with pure anatase crystalline structure was used as feedstock. The morphology and the crystal phase of the powder particles are shown in Fig. 2. The average particle size of the powder is about 20 μm measured by Microtrac Particle Analyzer (NIKKISO, Tokyo, Japan). The feedstock powder supplied using screw feeder (Nisshin Engineering, Tokyo, Japan). Grit blasted 100 mm × 50 mm × 5 mm soft steel (SS400) plate was prepared as substrate. The substrate is reciprocated by X-Y drive system during spraying in order to form a uniform thickness coating.

The crystal structure of the coatings is determined by x-ray diffraction (XRD: RINT-2200, Rigaku, Tokyo, Japan) with a CuKα radiation. The cross section microstructures of the coatings were observed by scanning electron microscope (SEM: JSM-6390, JEOL, Tokyo, Japan). The photocatalytic property of the coatings was evaluated by a NO_X elimination test illustrated in Fig. 3. Simulated contamination air is fed into a reaction chamber for 1 h. The contamination air includes 1 ppm of NO gas (measured by NO meter without UV irradiation) and 50% of humidity. The cold-sprayed TiO_2 coatings or the feedstock powder are placed in the reaction chamber. Both of these specimens are prepared in a same size. TiO_2 can work as a photocatalyst under UV irradiation. Thus, UV light is used in this evaluation. The samples were irradiated by ultraviolet light by using a black light having a power of 1.2 mW/cm^2 which is almost the same as

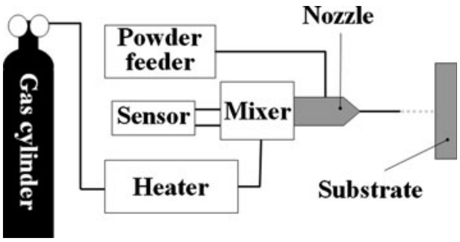

Fig. 1 Schematic of cold spray equipment

Table 1 Cold spray conditions

Gas nature	Helium	Nitrogen
Gas pressure, MPa	0.8	1.0
Gas temperature, °C	200, 300, 400	200, 300, 400
Spray distance, mm	10	20
Traverse speed, mm/s	20	20

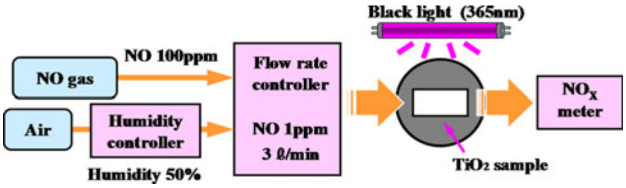

Fig. 3 Schematic diagram of the NO elimination test

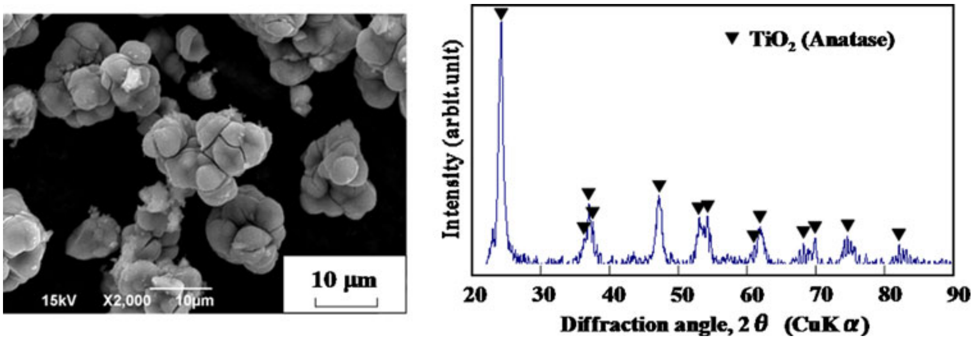

Fig. 2 Morphology and crystal structure of the TiO_2 feedstock powder

the sunlight (1-3 mW/cm^2). The NO elimination ratio is calculated by Eq 1 at 1 h irradiation.

$$E = \frac{[\mathrm{NO}]_0 - [\mathrm{NO}]_t}{[\mathrm{NO}]_0} \times 100, \qquad \text{(Eq 1)}$$

where E is the NO elimination ratio, $[\mathrm{NO}]_0$ is initial NO gas concentration (ppm), and $[\mathrm{NO}]_t$ is NO gas concentration with UV irradiation.

3. Results and Discussion

3.1 Spraying with Helium Gas

Figure 4 shows the cross section of cold-sprayed TiO_2 coatings using He as process gas. The thickness of the coatings increased with the gas temperature. The thickness of the coatings fabricated with 200, 300, and 400 °C is about 20, 25, and 50 µm, respectively. In previously published reports on the ceramic deposition by cold spraying (Ref 11-14), sprayed particles are mechanically embedded into the metallic substrate surface. Therefore, the thickness of the coating is smaller than the feedstock particle size. On the contrary, the thickness of the coatings produced in this study is approximately 100 µm with a temperature of 400 °C, which is much larger than the feedstock particle size. It indicates that the sprayed particles built-up a thick coating on the substrate, and reveals that the coatings consist of splats which are bonded to each other.

XRD spectra of the coatings are shown in Fig. 5. In the case of the coatings fabricated with lower gas temperature, substrate Fe peaks are appeared. It is due to the thickness of the coatings. Some peak shift can be observed in these coatings compared with feedstock powder. A residual

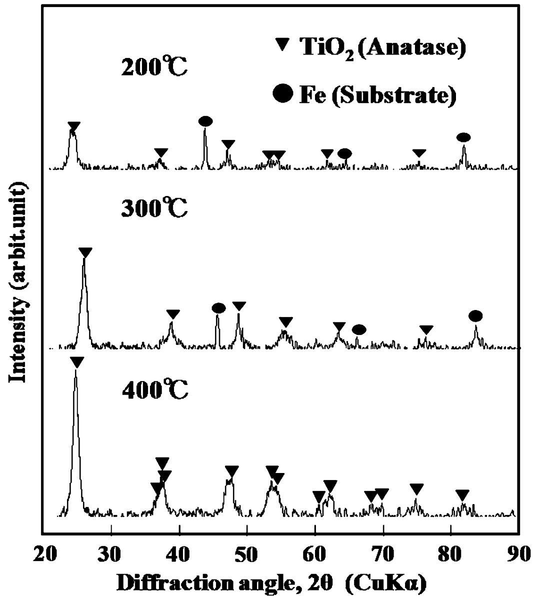

Fig. 5 XRD spectra of coatings sprayed with He

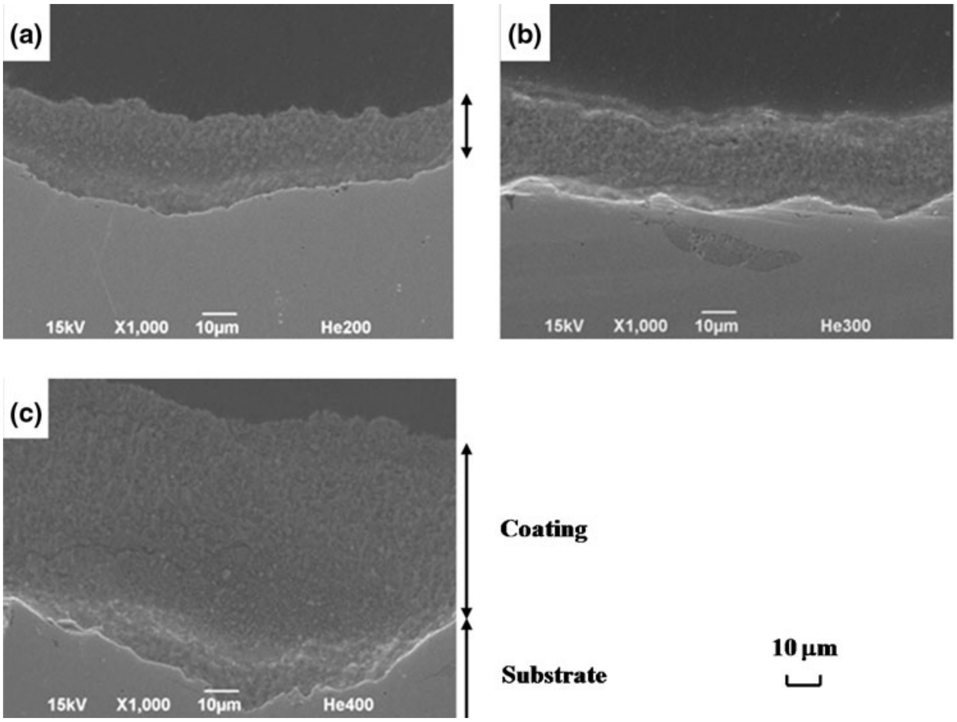

Fig. 4 Cross section microstructure of coatings sprayed with He. Spraying with gas temperature of (a) 200 °C, (b) 300 °C, and (c) 400 °C

stress in the coating might affect to the shift. However, the surface of the coatings is very rough. It also affected to the peak shift. Independently of the gas temperature used, all the coatings maintained the anatase crystal phase of the feedstock powder. The anatase phase of the feedstock powder never transformed into the rutile phase during spraying due to its lower heating temperature of cold spray process compared with other conventional thermal spray processes. For the highest gas temperature condition (400 °C), it is much lower than the phase transformation temperature (900 °C). Therefore, it is possible to fabricate anatase phase of thick TiO_2 coatings by cold spraying with using He process gas.

3.2 Spraying With Nitrogen Gas

Spraying with He as process gas has some advantages for the cold spray process such as increasing the particle velocity and decreasing the influence of plate shock. However, He is too expensive to use in industry, because in order to obtain such an ultrasonic stream, the cold spray process uses a large amount of process gas. We can use He recovery system on cold spray; however, this system needs chamber which confines the substrate size. Therefore, using a cheaper process gas is required for the cold spray process. However, spraying with N_2 as process gas which is a safe and cheap gas, might induce lower deposition efficiency and the possibility to obtain a coating compared with using He. TiO_2 coatings were fabricated using N_2 as process gas with similar gas conditions as the others used for the experiments with He as process gas (Table 1).

Figure 6 shows the cross section of cold-sprayed TiO_2 coatings using N_2 as process gas. It clearly reveals that TiO_2 thick coatings may be produced on the substrate. Cold spraying of TiO_2 coatings is also possible when using N_2 as process gas. It also shows that spraying with He as the process gas is not a main factor for thick layer formation of TiO_2 coatings using the cold spray process. The thickness of the coatings is observed for increased with the gas temperature as for the spraying with He. This result is similar to what the spraying of metal coatings using the cold spray process. For the metal coatings, the increase of the gas temperature influences the gas and particle velocity and the particle softening enabling an improved deposition of the sprayed particles. For the ceramic coatings, the softening of cold-sprayed TiO_2 particles could not be taken into account for the gas temperature regions. Therefore, only the influence of the gas temperature on the particle velocity and kinetic energy may be considered. These results show that the deposition efficiency of ceramic particles may be increased by controlling the process gas conditions as for the metallic coatings.

XRD spectra of the coatings are shown in Fig. 7. Some peak shift can be observed in these coatings same as Fig. 5. It is also considered to cause of residual stress and/or surface roughness. Independently of the gas temperature used, all the coatings maintained the anatase crystal phase of the feedstock powder, it was already observed for the spraying with He. The gas nature is not a main factor for the fabrication of TiO_2 coatings having an anatase structure. Furthermore, the spray conditions (gas pressure and temperature) are similar to the parameters normally

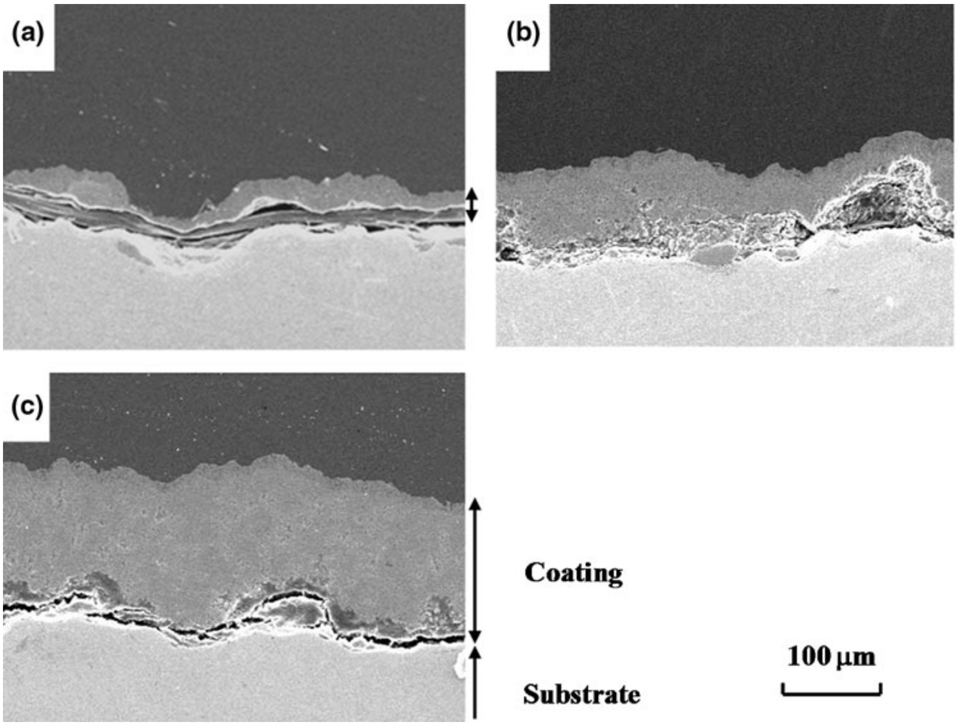

Fig. 6 Cross section microstructure of coatings sprayed with N_2. Spraying with gas temperature of (a) 200 °C, (b) 300 °C, and (c) 400 °C

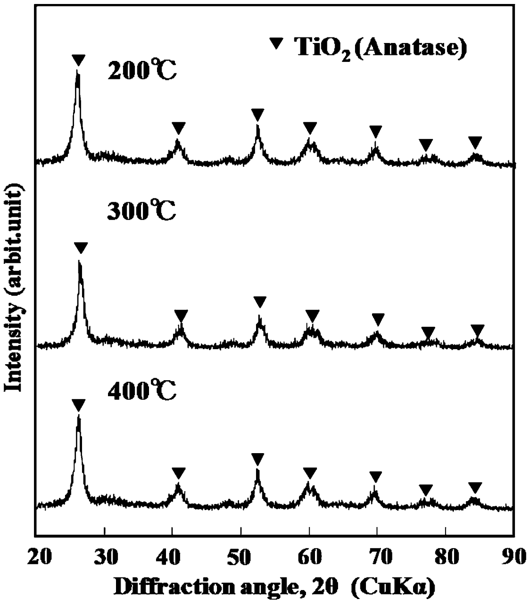

Fig. 7 XRD spectra of coatings sprayed with N_2

used for the spraying of metals. The deposition mechanism of cold-sprayed ceramic particles has not been clarified. However, these results prove that the process gas conditions are not a main factor for TiO_2 ceramic deposition and thick layer formation on cold spray process. It suggests that the feedstock powder is an important factor to fabricate a TiO_2 ceramic coating with an anatase structure.

3.3 Photocatalytic Property of Cold-Sprayed TiO_2 Coatings

The photocatalytic property of the cold-sprayed TiO_2 coatings is evaluated by the NO elimination test. The NO elimination ratio of the feedstock powder and the coatings produced with each gas condition are shown in Fig. 8. The NO elimination ratio of the coatings is higher than the feedstock powder apart from the coating sprayed with 200 °C of N_2. These samples exhibit an excellent NO elimination ratio which is around 80%. Since the coatings maintain the anatase phase of the feedstock powder as shown in the XRD results (Fig. 5 and 7), and that the coatings do not include any impurities such as a binder material, it is quite understandable that a similar photocatalytic property of the feedstock powder and the coatings is measured. However, most of the coatings exhibit a slightly higher NO elimination ratio than the feedstock powder. The deposition mechanism of cold-sprayed TiO_2 ceramic particles; however, some deformation or breakdown of the particle has to be occurred on the substrate in order to deposit. According to the deformation or breakdown of the feedstock particle, the surface area of deposited particle is increased compared with feedstock particle. A photocatalytic reaction is a surface reaction, thus the photocatalytic property is strongly affected by the surface area. In the consequence, the photocatalytic property of the coatings was higher than the feedstock powder.

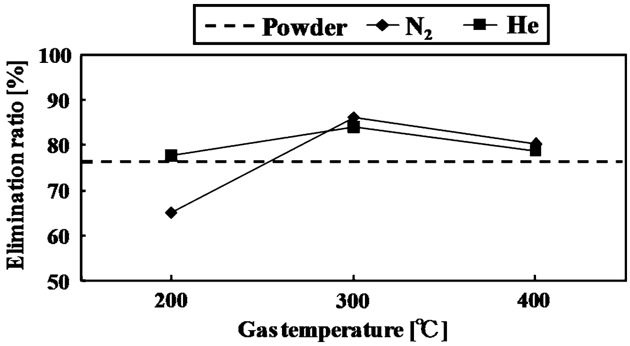

Fig. 8 NO elimination ratio of the feedstock powder and cold-sprayed coatings

The deposition mechanism is considered to be the same for all spray conditions. It means that the surface area of the coatings does not change significantly. Therefore, the NO elimination ratio may exhibit almost the same results for all coatings. However, the coating sprayed with 200 °C of N_2 exhibits lower elimination ratio. In this spray condition, the deposition efficiency of sprayed particles is low. The coating fabricated with lower gas temperature was not thick and uniform. To fabricate a TiO_2 coating by cold spraying which possess a good photocatalytic property, inexpensive N_2 can be used for the process gas with higher gas temperature. Concludingly, the cold spray process is an ideal process for the fabrication of a TiO_2 photocatalyst coating for large area applications.

4. Conclusions

In this study, TiO_2 photocatalyst coatings were fabricated by cold spraying while changing the process gas nature and temperature in order to understand the influence of the process gas conditions. TiO_2 coatings having an anatase phase could be successfully fabricated in all spray conditions used. The photocatalytic property of the coatings was evaluated. Consequently, the following conclusions can be drawn:

(1) TiO_2 coatings with an anatase phase of could be fabricated with both He and N_2 for the process gas and conventional gas pressure and temperature. Clearly, the process gas conditions are not a main factor for the deposition of TiO_2 ceramic particles.
(2) The coatings thickness was increased with the process gas temperature. The deposition efficiency of sprayed particles can be controlled by the process gas conditions. It is same as the cold spraying of metallic coatings.
(3) All coatings fabricated in this study exhibited an excellent NO elimination ratio. The process gas conditions for the fabrication of the coatings did not affect

the photocatalytic property. Inexpensive N_2 can be used for the process gas. Cold spraying is an ideal process for the fabrication of TiO_2 photocatalyst large area coating having an anatase phase.

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