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Article

Deposition of Photo-Catalytic TiO_2 Film by Low Power Atmospheric Suspension Plasma Spray Using Ar/N_2 Working Gas

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Abstract: As a photo-catalytic titanium oxide film deposition process, thermal spray is hoped to be utilized practically on the condition that it is relatively easy to deposit anatase rich films. However, because of its high equipment and feedstock powder costs, it is very difficult to introduce thermal spray equipment into small companies. In this study, to develop a low cost thermal spray system, low power atmospheric suspension plasma spray equipment with titanium hydroxide suspension created by hydrolysis of titanium tetra iso butoxide using Ar, N_2 as working gases. For avoiding sedimentation of the hydroxide particles in the suspension, mechanical milling of the suspension was conducted to create colloidal suspension before using it as feedstock. Moreover, an Ultrasonic wave container was used to keep the suspension particles moving while the spray process was conducted. After the film deposition, with As for the coating, anatase rich TiO_2 film could be obtained. For characterization of the film, microstructure observation by optical microscope and X-ray diffraction was carried out. Consequently, by creation of colloidal suspension, deposition could be conducted without sedimentation of the hydroxide particle in the suspension during operation. Besides it was proved the film had enough photo-catalytic property to decolor methylene-blue droplet.

Keywords: photo-catalysis, suspension plasma spray, thermal plasma, titanium oxide

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1. Introduction

TiO_2 is almost the only material suitable for industrial use at present, and probably in the foreseeable future as well. This is because TiO_2 has the most efficient photo activity, the highest stability, and the lowest cost [1]. Various deposition techniques can deposit thin titanium oxide films for photo-catalytic applications (anatase–TiO_2, etc.). For example, sputtering [2], metalorganic chemical vapor deposition (MOCVD) [3], spray pyrolysis [4], the sol-gel process [5], thermal spray [6], and various other methods. However, there are several engineering problems associated with these deposition processes, such as the necessity of vacuum equipment, low deposition rates, deposition time, the requirement of special and costly equipment, as well as feedstock powder [7]. In this study, the purpose is to develop a low cost thermal spray system and low power atmospheric suspension plasma spray equipment. A thermal spray process for photo-catalytic titanium oxide coating was fabricated using 1 kW class Atmospheric Suspension Plasma Spray (ASPS) equipment. Ar and N_2 are mostly used for their mass, while the secondary gases (He and H_2) were used for their thermal properties [8]. Since Ar is a costly gas, a low running cost deposition condition such as using a low cost N_2 dominant working gas was required. Feedstock material was created by hydrolysis of titanium tetra iso butoxide using Ar and N_2 as working gases. In order to avoid sedimentation of the hydroxide particles in the suspension, mechanical milling of the suspension was conducted to create a colloidal suspension before using it as feedstock. A new Ultrasonic wave container was used to keep the suspension particles moving while the spray process was conducted. In this study, in order to develop 1-kw-class ASPS equipment, Ar/N_2 were used as the working gases as well as the

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photocatalytic titanium oxide film deposition made by using the ASPS equipment which we developed.

2. Materials and Methods

Fig. 1 shows the schematic diagram of the thermal spray equipment used in this study. This equipment consists of plasma torch, DC power source, feed-stock using ultrasonic supplying system and working gas supply system. Table I shows the deposition conditions. The tools used for mixing titanium oxide with water are shown in **Fig. 2**. They consist of a microfilter, a mixer, and a

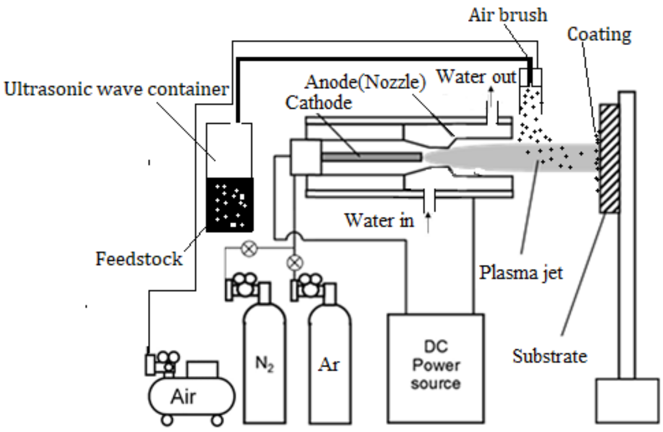

Fig.1 Schematic diagram of the suspension plasma spray (SPS) equipment.

Table 1. Suspension plasma spray parameters used to deposit the TiO_2 coatings in this study.

Process Parameter	Value
Sandblasting realized	Always
Working gas composition	Ar/N_2
Working gas flow rate, L/min	Ar 5 /N_2 0.136
Spray distance, mm	40–120
Discharge current, A	50
Constrictor diameter of plasma torch nozzle, mm	8
Feedstock	$Ti(OH)_4$ suspension *
Feedstock spray port, diameter, mm	7
Deposition distance, mm	40-80-120

* Created by hydrolysis of titanium tetraisobutoxide (TTIB, $Ti(OC_4H_9)_4$) (volume ratio of TTIB/H_2O = 8/70).

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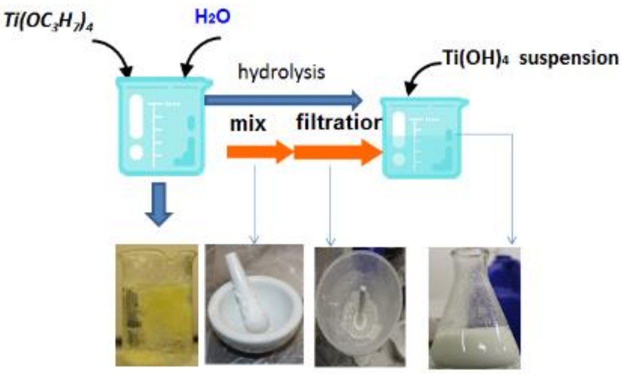

Fig.2 The shape of submicron particles mixing equipment.

special container (mortar and pestle) for mixing as well as for crushing and grinding. An amount of 2 mL of TTIB is diluted with stable water, and 20 mL of water is added to the TTIB and mixed to form submicron particles. The hydrolysis and condensation reactions can be summarized as follows: *Hydrolysis: $Ti(OC_4H_9)_4 + 4H_2O \rightarrow Ti(OH)_4 + 4C_4H_9OH$ (1) *Polymerization and crystallization (in the plasma jet and on the substrate): $Ti(OH)_4 \rightarrow TiO_2 + 2H_2O$ (2). An ultrasonic container uses a ceramic diaphragm vibrating at an ultrasonic frequency (0.5 - 1.7 MHz) to agitate the suspended particles **Fig. 3** and raise the temperature of suspension until 70 °C **Fig.4** while spray

Fig. 3 Appearance of the suspension particles located at the bottom of the container (a) before agitate the suspended particles and (b) after agitate suspended particles using ultrasonic waves.

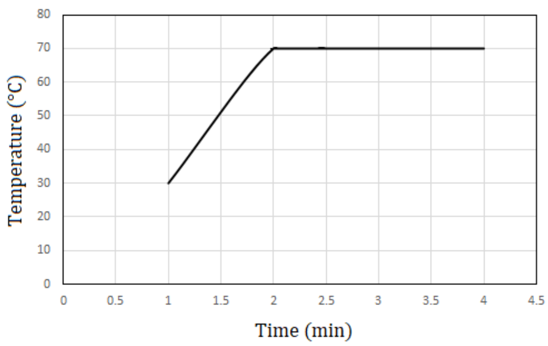

Fig. 4 Temperature of liquid (suspension) as a function of time on the frequency of 2.4MHz.

to the plasma jet **Fig. 5.** The spray method was external spray using an airbrush atomization feeding system where the suspension is first atomized and sprayed into the plasma jet **Fig.6-5**. Three hundred and four 15 × 15 × 1 mm stainless steel plates polished surface was used as the substrate.

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The substrate was horizontally set on the substrate **Fig. 1** holder, and the central area of the sample was placed perpendicular to the axial center of the plasma jet. The spray distance (the distance between the nozzle outlet of the plasma torch and the surface of the substrate) was varied

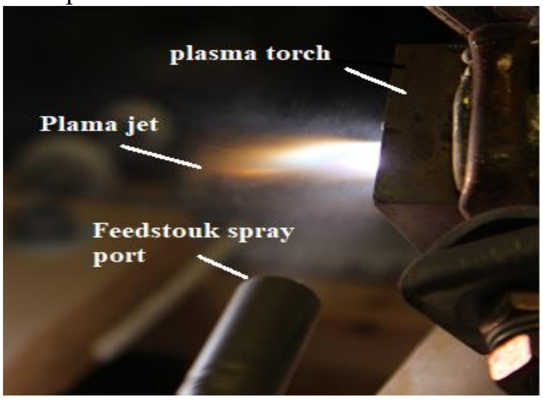

Fig. 5 Appearance of the external feedstouk sprat to the plasma jet.

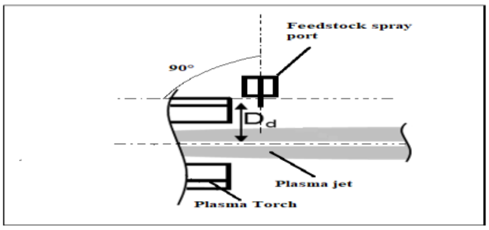

Fig. 6. Configuration of the suspension plasma spray torch with Illustration of the feedstock spray port.

from 40 to 120 mm. The deposition time was 15 min. The input power for discharge was fixed at 50 A. Deposition temperature (the substrate temperature during the film deposition) was measured by a thermometer (IGA-CST2, LEC Co. Ltd.). After the titanium oxide film deposition, the microstructures of the films were investigated by X-ray diffraction (CuKa, 40 kV, 100 mA). In order to confirm photocatalytic property of the film, methylene-blue wettability and decoloration test using UV irradiation equipment (**Fig. 7**) were carried out.

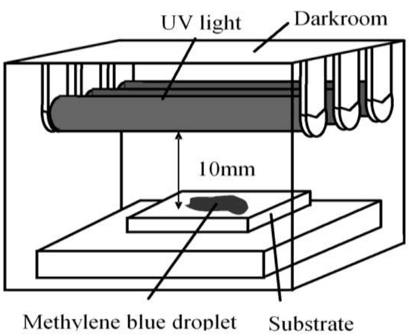

Fig. 7 Schematic diagram of the equipment used in methylene-blue decoloration test.

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3. Results

One of the challenges of our research was the problem of TiO_2 particles settling to the bottom of the spray hopper while spraying. The settling particles had a strong tendency to clog inside of the external sprayer nozzle and reduce the quality of the coating achieved or stop the spray entirely. In order to eliminate clogging, we had to develop a new kind of ultrasonic container to thoroughly suspend TiO_2 particles, which could be used while spraying **Fig. 8**.

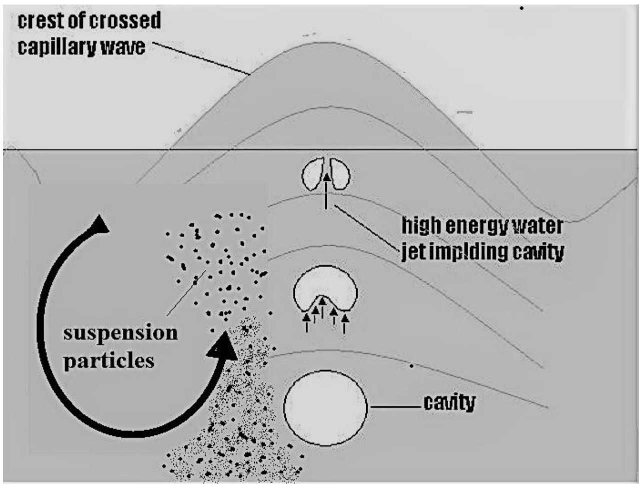

Fig. 8 Mechanism of movement for the suspension particles during exposure to the ultrasonic wave.

This container uses ultrasonic vibrations at 0.5MHz to 2.4MHz to vibrate the TiO_2 particles in the suspension. Vibration is started at 0.5MHz and the frequency is increased gradually to 2.4MHz to prevent excessive splashing. Vibrating at 2.4MHz ensures uniform suspension of particles. As a side effect of the vibration, the suspension temperature is raised by either friction or cavitation from 40 °C to 70 °C **Fig.4**. Spraying is commenced once the suspension reaches 70 °C.
Substrate temperature: In our experiments, we found that the substrate temperature was quite low, the surface temperature increases with decreasing the spraying distance **Fig. 9**.

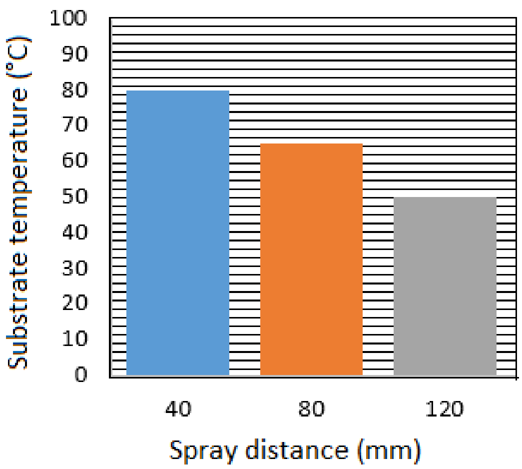

Fig. 9. Substrate temperature as a function of distance.

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In the case of d=40 mm the substrate temperature was 80°C and d=80 mm was 65°C d=120 was 50°C which enables this coating to be sprayed on materials sensitive to heat damage. Spraying this coating on glass, for example, should present no risk of damage. Despite the high temperature of the plasma jet, due to the effect of heat transfer when the suspension is aerosolized, the temperature at the surface of the substrate is significantly reduced. In our previous study, we found that the addition of N_2 increased the thermal energy of the Ar plasma jet. However, in the previous study, N_2 was used at a rate of 2.5L per minute, whereas in this study N_2 was used at a rate of 0.1L per minute, representing a significant reduction in cost.

In general, when working with Ar plasma jets, the thermal energy increases with increased Ar working gas flow rate. However, in this case, the thermal energy of the jet decreased as a result of the working gas being a mixture of Ar and N_2. This is critical as high temperature is needed in order to change the TiO_2 particles from the amorphous to the anatase phase, but not so hot as to damage the substrate. By using this Ar / N_2 mixture, we are able to achieve high In general, when working with Ar plasma jets, the thermal energy increases with increased Ar working gas flow rate. However, in this case, the thermal energy of the jet decreased as a result of the working gas being a mixture of Ar and N_2. This is critical as high temperature is needed in order to change the TiO_2 particles from the amorphous to the anatase phase, but not so hot as to damage the substrate. By using this Ar / N_2 mixture, we are able to achieve high thermal energy at the front of the plasma jet, but lower the energy near the substrate, allowing for low substrate temperature.

Although low substrate temperature usually impedes photocatalytic film, in our experiments we were able to spray at 40mm and still achieve excellent photocatalytic film **Fig. 10. Fig. 10** shows

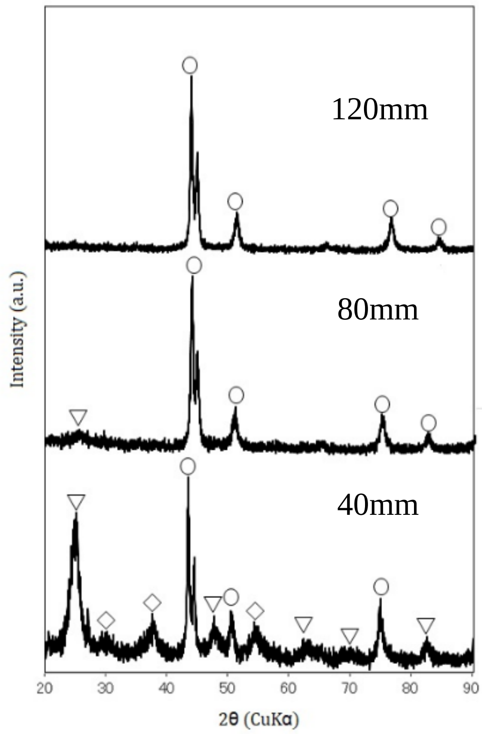

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Fig. 10. XRD patterns of the samples. (△: anatase, ◇: rutile,○ : Fe(substrate)).

XRD patterns of the films deposited at the different deposition distance using. A white color film with smooth surface was obtained with deposition distance of 40 mm. And also, a white color film with coarse surface was deposited with deposition distance of 80 mm. According to the XRD results, though well crystallized anatase and rutile were included in the film deposited with deposition distance of 40 mm, the degree of crystallinity of the film decreased with increasing deposition

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distance. Finally, amorphous TiO_2 film was deposited with deposition distance of 120 mm We achieved good photocatalytic results at 40mm. At 120mm however, the coating was amorphous and the plasma jet lacked sufficient power to effectively provide the substrate with a photocatalytic coating.

Fig. 11 shows the optical micro graphs of the surface and fracture cross-section of the titanium oxide film deposited sample on the condition of 40 mm. As shown in this figure, a porous structure film was deposited. On the conditions of 40 and 80 mm, films with almost the same microstructure

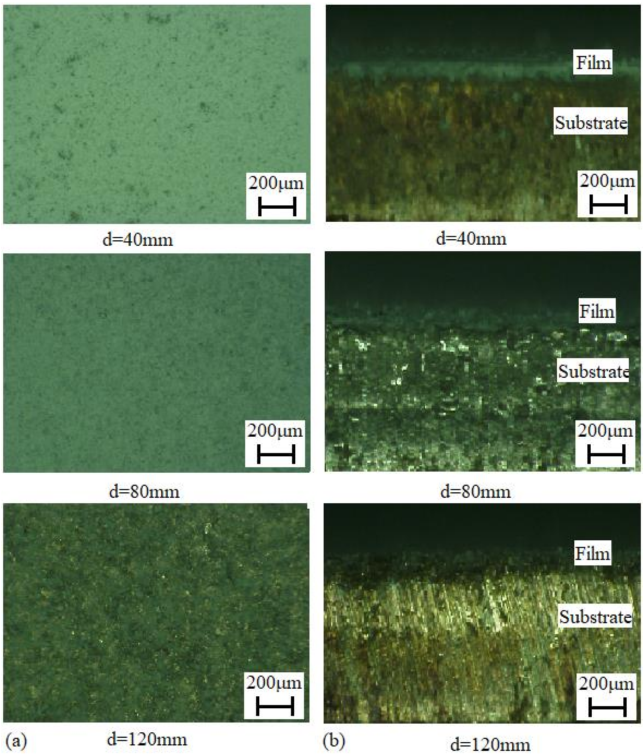

Fig. 11 Optical micrographs of the cross sections and surface morphologies of the titanium oxide films deposited on all distance. (a) Cross-section. (b) Surface morphology.

were deposited. The film with almost uniform thickness distribution could be obtained on any conditions. Furthermore, this film had enough photo-catalytic property to show decolor the methylene blue perfectly by 20 h ultraviolet irradiation, which is shown in **Fig. 12**.

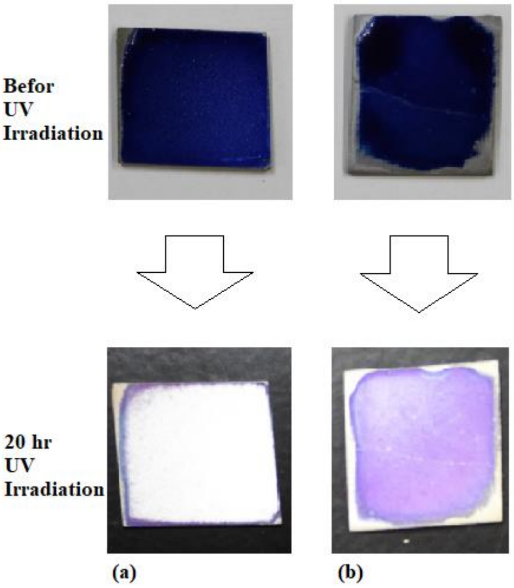

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Fig. 12 Results of methylene blue decoloration test. (a) d = 40 mm. (b) d = 80 mm.

In order to measure photocatalytic properties, we conducted UV radiation testing and a decoloration test using methylene blue. By observing the decoloration of the coating, we were able to conclusively determine the photocatalytic activity of the film. At both 40mm and 80mm spray **Fig. 12.** distances we found excellent photocatalytic properties. We stained a coated sample with methylene blue, after 20 hours of UV irradiation the decolorization was complete, with measurements confirming degradation at spray distances of 40mm and 80mm **Fig. 12**. From these results, it was proved that highly crystallized film could be deposited in distance of 40mm by perfect vaporization of suspension particles starting material spray to the plasma jet using newly developed system.

4. Conclusions

In order to develop low cost materials that can be used for the titanium dioxide film deposition process, deposition of high-rate film using low cost materials was carried out. Thick photo-catalyst film was obtained using an atmospheric suspension plasma spray with external spray as a fabrication process. Consequently, excellent photocatalytic film was obtained, and it was confirmed that the anatase films had photo-catalytic properties by using a methylene-blue droplet test and its decoloration test. This new system by using ultrasonic waves to spray the suspension particles to the plasma jet proved successful in coating high-quality photocatalytic film. From these results, this low cost starting material with new atmospheric SPS has the potential for a high rate and low cost, functional, oxide film deposition.

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