Preparation of Plasma Sprayed Titania/Hydroxyapatite Photocatalytic Coatings with Nanostructured Powder

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Abstract

Anatase phase Titanium dioxide has a photo-catalytic performance for environmental protection. In this study, titanium dioxide/hydroxyapatite photo-catalytic coatings were deposited by atmospheric plasma spraying using powders with nano-sized grains. The injecting position of powder was varied in order to prepare porous structure coatings with high photo-catalytic activity. The phase compositions and microstructures of the coatings were characterized using X-ray diffraction (XRD) and Field Emission Scanning Electron Microscopy (FESEM). The results showed that the porous structure coatings with relatively high anatase content could be obtained by controlling the injecting position of the powder. The bimodal microstructure of the coatings was also controllable.

Keywords: (TiO_2/HAP); (Plasma spraying); (Phase composition); (Photo-catalysis)

1. Introduction

Environmental pollution has been recognized as a serious problem in the last decades. Both wastewater treatment and purification of polluted air have attracted extensive attention by many researchers. Photo-catalysis is one of the effective ways to degrade harmful organic pollutants to human body [1,2]. Among those photocatalysts, such as TiO_2, ZnO, WO_3 and Fe_2O_3; TiO_2 is known to be the best photocatalyst owning to its excellent photocatalytic activity, physical and chemical stability and non-toxicity [3]. TiO_2 crystals has three different phases: anatase, rutile and brookite [4]. The brookite phase has not been studied as a photocatalyst due to having many defects in its crystal structure. The anatase phase has a tetragonal structure and from the viewpoint of thermodynamics it is a metastable phase. The rutile phase has tetragonal structure and it is stable at high temperature [5]. Anatase should transform to rutile phase at temperature above 1180K. The photocatalytic performance of anatase is generally considered to be superior to that of rutile.

Thermal spray technique have been applied to deposit a wide variety of coatings. Recently, the investigation of plasma spraying using anatase powders has been performed for producing TiO_2 coatings containing anatase phase [6]. This is due to the fact that anatase TiO_2, as a photo-catalyst, has significant influence on the environmental purification. Anatase TiO_2 tends to form rutile during the plasma spray process since powder is injected into the high temperature zone of the plasma jet. TiO_2 coatings containing anatase can be only accomplished by means of controlling the plasma spraying process in which partially melted anatase particles embed within the coatings [7]. Therefore the new technological method is fundamentally important to reduce the transformation from anatase to rutile phase during solidifying.

One of the authors has developed a high power plasma jet, which was called gas tunnel type plasma jet, and the performances were clarified in previous studies [8-10]. It is superior to other conventional type plasma jets and has great possibilities for various applications to thermal processing [11]. As to the formation of high performance materials, high quality ceramic coatings were obtained by the gas tunnel type plasma spraying method [12,13]; for example, typical alumina coating produced with a Vickers hardness of Hv=1200-1600 [14]. As another application, the gas tunnel type plasma jet was applied to the surface nitridation of titanium. This experiment also investigated the possibility of the speedy formation of a highly functional thick TiN coating [15].

It was reported that grain size plays a role in the photo-decomposition efficiency of organic pollutants for the TiO_2 photocatalyst [1]. Because the TiO_2 photocatalytic reaction occurs on powder surface, as the grain size becomes smaller, the specific surface area becomes larger and the degradation efficiency of organic pollutants also increases. Therefore, the photodecomposition efficiency of coatings with nano-size TiO_2 powder can be higher than that of normal micro-size powder. It has been pointed out that hydroxyapatite (HAP), used as biomaterial, has a significant characteristic of the absorption of organic pollutions. The specific powders containing TiO_2 and HAP contents can improve the photodecomposition efficiency to a certain extent.

† Received on May 31, 2002

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Transactions of JWRI is published by Joining and Welding Research Institute, Osaka University, Ibaraki, Osaka 567-0047, Japan

In this study, a new technological method was attempted during the spraying process with synthesized nano-TiO_2/HAP powders. The injection tube of the powder was set at different positions along the axial direction outside the plasma torch. Microstructures of the sprayed coatings were characterized using Field Emission Scanning Electron Microscopy (FESEM). The effect of injection position on the porosity and crystalline phases of the TiO_2/HAP coatings were investigated and analyzed.

2. Experimental

2.1 Plasma spraying and powder used

During the plasma spraying process, phase evolution of the anatase-TiO_2 has to be imagined because both photo-decomposition reaction and photo-activation [1] largely depend on the anatase phase. Therefore, the phase composition of the TiO_2/HAP coatings might be changed through injecting the powder to the different temperature zones of the plasma jet. The TiO_2/HAP coatings were prepared using the gas tunnel type plasma spraying torch which has been described in detail elsewhere [16]. As shown in **Fig.1**, the feedstock powder was vertically injected into the plasma flame at the position of 5, 15, 25, 35mm, respectively from nozzle, and 5mm from the edge of plasma jet in this study. Stainless steel plate with a dimension of 50×50×3mm was employed as a substrate. Prior to spraying, the substrate was grit-blasted using SiC powders and cleaned with acetone. The traverse times of the substrate related to the plasma jet were 4 passes. Argon-cooling of Q=80l/min was used from the back of the substrate. The details of experimental conditions are summarized in **Table 1**.

TiO_2+30vol. %HAP powder with particle size of -45+10μm was used. **Figure 2** shows SEM image of the nano-structured TiO_2/HAP particle and EDS analysis result. Each TiO_2/HAP particle is formed by an agglomeration of various individual nano-sized particles of TiO_2 and HAP. EDS analysis shows that Ti, Ca, O, P existed in the interior of individual particles.

2.2 Characterization of the coatings

A Field Emission Scanning Electron Microscopy (FESEM) with an acceleration voltage of 20kV was used to observe the morphology of the sprayed coatings. The phase composition of the coatings was conducted by X-ray diffractometer (JEOL JDX-3530M) at 40kV and 40mA. Scans were run from 20° to 80° with a 2θ step of 0.02° and a time increment of 1.00s. A copper target was used as X-ray source using Kα Cu radiation with the wavelength of 1.5418A. The porosity was calculated on the polished cross-section through optical microscopy, in conjunction with a digital camera and image analysis software. The anatase content ratio in the coatings was estimated using the following equation [4]:

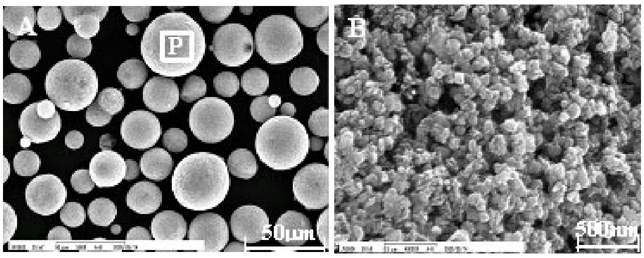

Fig.2 SEM image of TiO2-HAP micro-structural poweders formed by the agglomeration of individual nano-sized particles ; EDS analysis results for point P.

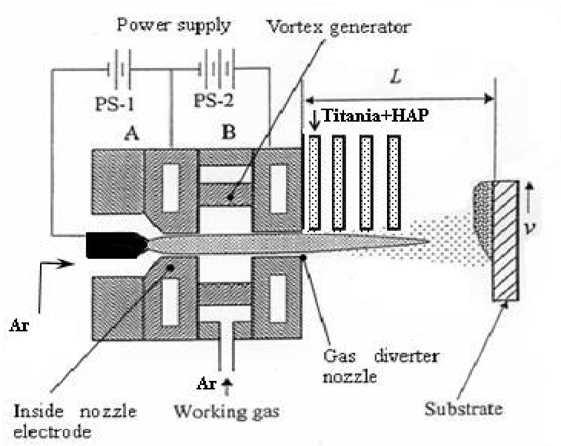

Fig.1 Experimental Schematic of gas tunnel type plasma spraying torch with injection positions (IP) of 5, 15, 25, 35mm, respectively from the nozzle exit.

Table 1 Experimental conditions:

Power input P: (kW)	14.7-15.4
Pass N: (times)	4
Working gas flow rate Q:(Ar) (ℓ/min)	180
Spraying distance L: (mm)	100
Carrier gas flow rate: Ar (ℓ/min)	10
Environmental gas flow rate:(N_2) (ℓ/min)	80
Powder feed rate: (g/min)	9.5

$$R_{A\text{-}TiO_2} = \frac{I_{A-TiO_2}}{I_{A-TiO_2} + I_{R-TiO_2}} \times 100\% \qquad (1)$$

where $R_{A\text{-}TiO2}$ is the anatase content ratio, $I_{A\text{-}TiO2}$ is the intensity of the (101) peak for anatase and $I_{R\text{-}TiO2}$ is the intensity of (110) peak for rutile, respectively.

The photo-catalytic performance of the coatings was evaluated by calculating the anatase content ratio in the coatings at different injecting positions.

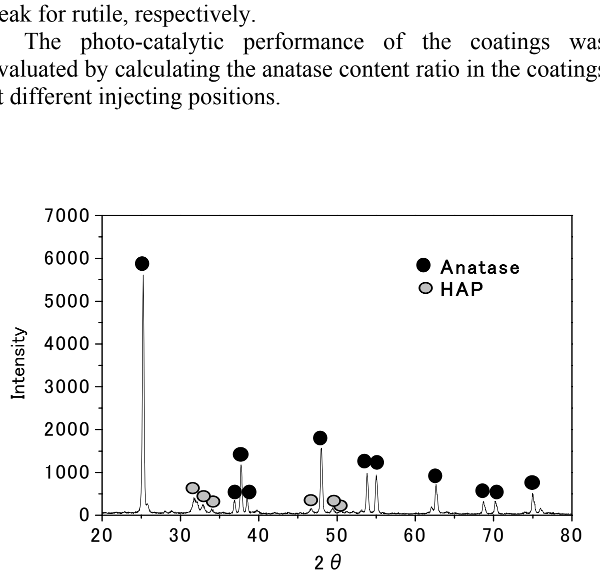

Fig.3 X-ray diffraction pattern of TiO2-HAP powder.

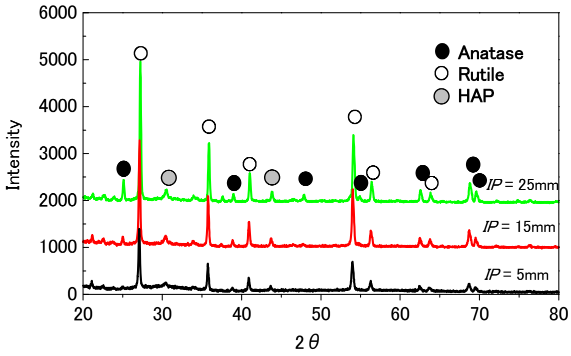

Fig.4 X-ray diffraction patterns of TiO2-HAP coating surface with *IP*=5, 15, 25, 35mm, respectively.

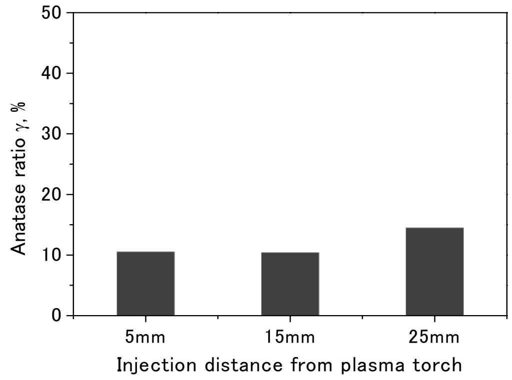

Fig. 6 Effect of injected position on the anatase content ratio in the plasma sprayed coating.

3. Results and Discussion

3.1 Crystalline phase and porosity

Fig.3 shows the X-ray diffraction patterns of the powder of titanium dioxide/hydroxyapatite. After spraying, the X-ray diffraction patterns of the coating deposited at the various injection positions were measured, and results were shown in **Fig.4.** It is seen that the coating surface mainly consisted of both anatase and rutile phases.

Fig.5 shows the anatase ratio in the coatings versus. the injected position. The anatase ratio increased with increase in the injected distance from the exit of the nozzle. In comparison with the previous result, the anatase ratio in the coating sprayed at *IP*=25mm is approximately homologous. The previous coating, containing 15% anatase phase by weight, and showed good photo-catalytic performance [7].

In addition to the anatase phase within the coating, the porous microstructure of the coating also plays an important role in improving the photo- catalysis reaction. The relationship of porosity in the coating and the injection distance from the exit of the torch nozzle was shown in **Fig.6**. It indicates that porosity of the coatings was increased with an increase of the injected position of the powder. The porosity of the coating at *IP*=25mm is beyond 40% by volume. A larger porosity can enhance the photo-catalytic performance of the coatings by increasing the reacting area [17]. The plasma sprayed coatings, having both considerable photo catalytic activity and porous structure, could be formed successfully by controlling the injected position of powder with nanostructure particles. As the thickness of coatings at *IP*=35 is very thin and too weak, the comparison with the coatings up to *IP*=25mm was difficult.

3.2 Coating characterization

Fig.7 A, B shows microstructure of the cross section of the sprayed coatings at *IP*=5mm and 15mm, respectively. The cross–section of the coating sprayed at the first position (*IP*=5mm) exhibits the lamellar structure containing few pores in the interior of the lamellas. However, **Fig.7 B** at *IP*=15mm presents a higher porosity in comparison with **Fig.7 A** and a nanostructure zone is found (**Fig.7 C**). The rectangle area (**Fig.7 C)** shows porous form (**Fig.7 D**), like the structure of TiO_2/HAP powder particles (**Fig.3 B**). It is thought that **Fig.7 C** shows that the un-melted and partially melted particles of TiO_2/HAP powders collide with the substrate during spraying. The individual nano-sized particles of the powder were rounded,

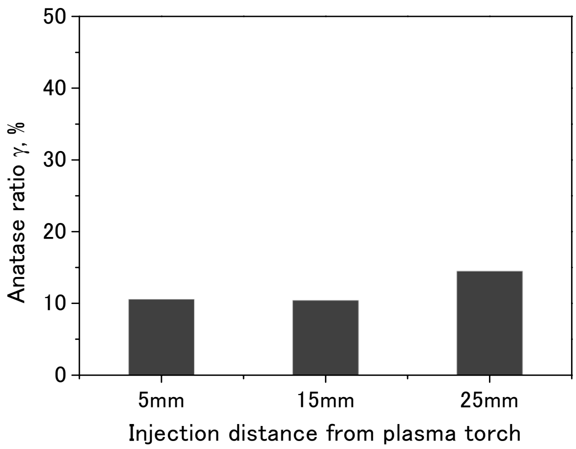

Fig. 5 Effect of injecting position on the anatase content ratio in the plasma sprayed coating.

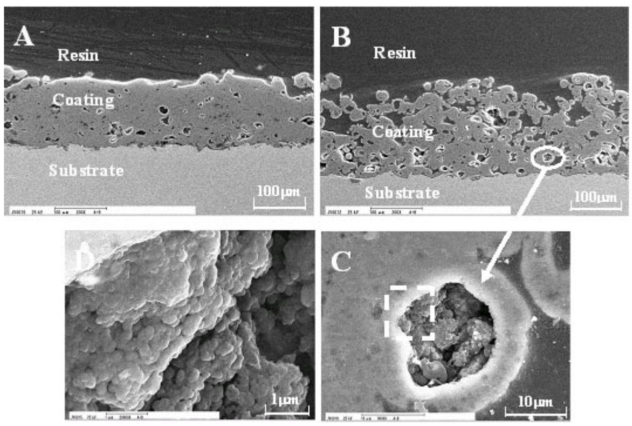

Fig.7 Typical lamellar structure A and porous-structure B on the cross-section of the sprayed coatings at *IP*=5, 15mm, respectively; D shows a pore and nano-particle structure of rectangle area of figure C.

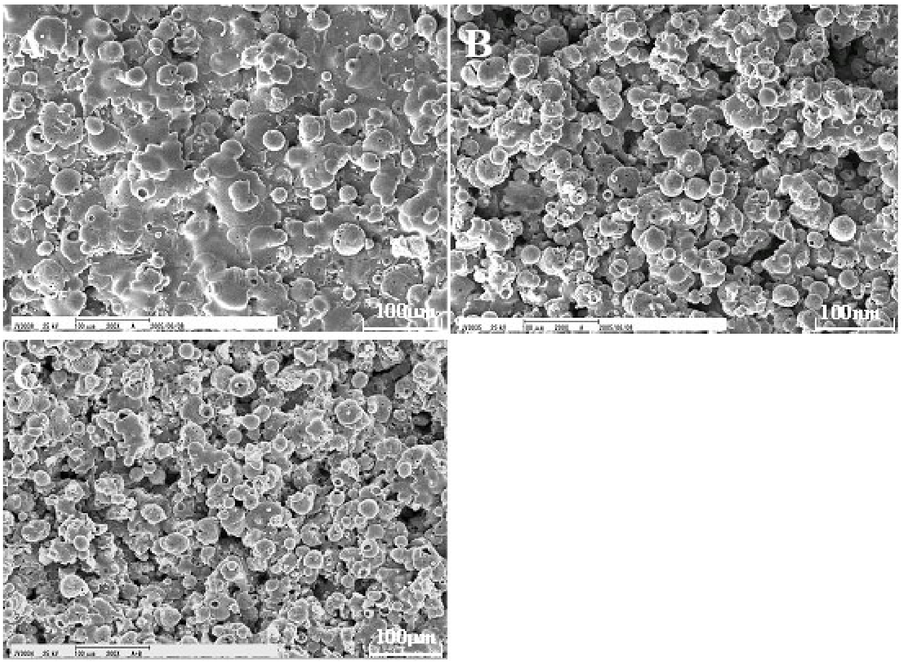

Fig.8 Coating surface morphology with different injection positions. A,B,C: *IP*=5, 15, 25, mm, respectively.

but they did not coalesce on the substrate. Therefore the porous structure of the agglomerated powder did not change the shape. [17]. It can be concluded that the microstructure of the sprayed coatings may be controlled by adjusting the injection position of powder.

Figure 8 shows the surface morphology of the coating deposited at *IP*=5, 15, 25 mm, respectively. As shown in **Fig.8 A**, the surface layer exhibits the typical flattened lamellar structure from which it can be considered that the nano-structured particles have been fully melted and accelerated and then deposited onto the substrate, followed by flattening, rapid cooling and solidification. The nano-sized agglomerated particles changed to micro-sized flattened layers on the coating. The property of this coating may be similar to the 'conventional' coating deposited using micro-sized particles. **Fig.8 C** shows the porous structure with many spherical particles on the surface of the coatings, and the magnified nano structure is shown in **Figure 9.** It is seen that the spherical particles were partially melted and combined with other particles. This porous structure is desirable for improving the photo-catalytic reaction of anatase-TiO_2.

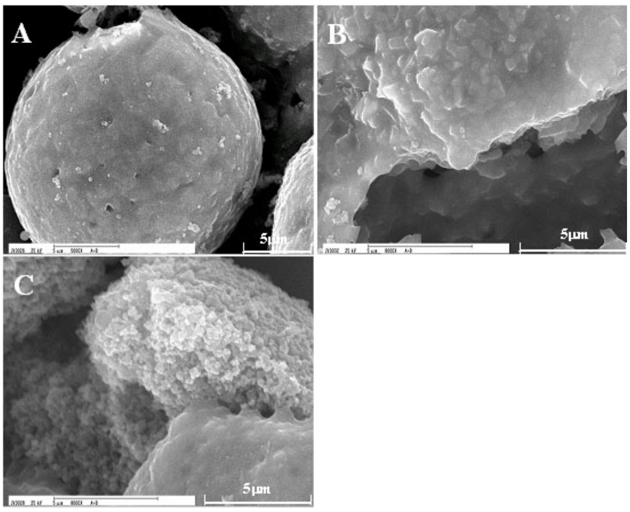

Fig.9 Coating surface morphology with the different injection position and nano-particles jointing structure sprayed by plasma jet: A the partially melted particle with *IP*=25mm, B the internal structure of partially melted particle with *IP*=25mm, C the jointing mode of unmelted and partially melted particles with *IP*=25mm, nano-particles morphology on the unmelted surface.

Fig.9 A, B, C shows the melted state of an individual particles and the variety of joining configurations of partially melted particles and un-melted particles. The agglomerated particle can keep the spherical shell after processing, as shown in **Fig.9 A**. This probably can be due to the powder which was injected in a relatively high temperature zone at a short injection position related to the substrate. Therefore, the particle with nano-sized grains melted on the particle surface during plasma spraying [18].

The partially melted particle appears to have the broken shape as shown in **Fig.9 B**. The solidified shell and un-melted core were exhibited in the partially melted particle, due to a temperature gradient distribution from the shell to the core. In addition, the low thermal conductivity of agglomerated nano-particles resulted from high porosity coating [18]. **Fig.9 C** shows the combination of partially melted and un-melted particles. The un-melted particles with agglomerated nano-sized grains can be combined in the melted particles. Therefore, anatase content ratio in the coating is increased with increasing the adhered un-melted particles in the surface of the coating. Therefore, the TiO_2/HAP particles with nano-size grains can en hance the photo-catalytic property.

This complex microstructure was in conformity with that of particles treated by plasma jet, and related to the different melting degrees of the nano-structured particles resulting from the synergetic effects of grain size and temperature heterogeneity of the plasma jet [19-20]. The reason seems to be the pressure of the gas in the particle with porous structure generated a thermal expansion to the outside which breaks the surface shell of agglomerated nanostructure particles [21].

4. Conclusions

TiO_2/HAP photo-catalytic coatings were prepared by plasma spraying using agglomerated powders with anatase phase. The sprayed coatings were mainly composed of both anatase and rutile phases.

1) The porosity and anatase content ratio in the coatings were increased with the powder injected in the relatively low temperature zone.
2) There exist both splats and many partially melted particles on the surface of the coatings sprayed at *IP*=15, 25mm. This ensures the plasma-sprayed coatings can exert higher photo-catalytic activity.
3) The 'complex microstructure' with two types of particle state can improve the mechanical properties of the nano-sized coatings, by optimizing the injection position of powder.

Acknowledgements

The authors would like to thank Dr. JiaLiang Zhang in Da Lian university of technology for his advise in experiment.

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