IOP Conf. Series: Materials Science and Engineering **114** (2016) 012031 doi:10.1088/1757-899X/114/1/012031

High Anatase Rate Titanium Dioxide Coating Deposition by Low Power Microwave Plasma Spray

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Abstract. Titanium dioxide is a promising photocatalyst material because of the magnificent properties of this material where it is able to remove the air pollution substance and the deodorizing function. Generally, the deposition method of a titanium dioxide coating is carried out by an organic system binder but the powerful photocatalytic reaction will degrades the binder. Therefore, thermal spray is considered to be the alternative method but this method will induce crystallization transformation of titanium dioxide from anatase phase with high photocatalytic activity to rutile phase with low photocatalyst which caused by high heat input. Since our microwave plasma spraying device is operable at low power comparing with conventional high power plasma spray, the reduce effect of the heat input onto the particles at the time of spraying can be achieved and coating deposition with high rate of anatase phase is expected. Therefore, in this research, the coating deposition by controlling the heat input into the spray particle which can be resulted in high rate of anatase phase with high photocatalytic activity was conducted. By controlled condition, coating with optimum anatase rate of 83% is able to be fabricated by this method.

1. Introduction

Titanium dioxide is a photocatalyst material which has been focused in recent studies because of the magnificent properties of this material where it possesses photocatalytic activity such as the ability to remove the water pollution substance as well as the deodorizing function [1, 2]. Photocatalyst is a material that alters the rate of a chemical reaction when exposed to light. There are various materials that show photocatalytic capability, and titanium dioxide is said to be the most effective [3]. From the high photocatalytic activity that it possesses, this material is being used for wide area of applications, from the construction field to the medical field.

Generally, the deposition method of a titanium dioxide coating is carried out by the fixation of titanium dioxide powder with an organic system binder. However, due to the powerful photocatalytic reaction of a titanium dioxide, it will let the fast degradation of the organic binder [4]. Therefore, from the recent studies, thermal spray is taught to be the alternative method to fabricate titanium dioxide coating with high photocatalytic activities. However, this method will cause high heat input and induces transformation from anatase phase with high photocatalytic activity to rutile phase with low photocatalytic activity [5]. The coatings produced by conventional plasma spray with input power of

28 kW possess low value of anatase content rate at approximately 40 %, and due to this, the study of the coating deposition methods which are able to restrain the phase change of spray particles is advancing [6].

Since our microwave plasma spraying device [7] is operable at low power (below 1 kW) comparing with conventional plasma spraying equipment, the control effect of the heat input to the particles at the time of spraying can be considered, and coating deposition with high rate of anatase phase is expected. Therefore, in this research, the coating deposition by controlling the heat input into the spray particles which can be resulted in high rate of anatase phase with high photocatalyst activity was conducted. In this study, the objective is to investigate the controlling factor for the change of phase composition of titanium dioxide by using microwave plasma spray.

2. Experimental procedures

2.1 Process and materials

2.1.1 Process

The experimental system of the atmospheric pressure microwave plasma spray is shown in Figure 1. Microwaves of 2.45GHz are transmitted through a rectangular waveguide and oscillated into a cylindrical resonant cavity by a hollow antenna on the axis. Working gas of Ar is mixed with spray particles in an aerosol chamber and supplied axially through the antenna. The system generates high-intensity electric field on the tip of the antenna, induces electrical breakdown of working gas, and plasma plume is generated at the downstream. The spray particles are heated and accelerated by the plasma plume, and the coating is deposited by the impact of spray particles onto substrate surface at downstream. Experimental condition for titanium dioxide coating deposition is shown in Table 1.

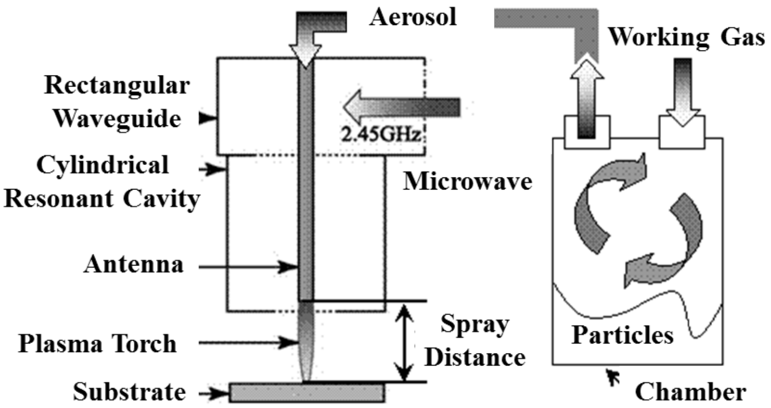

Figure 1. Schematic diagram of low power atmospheric pressure microwave plasma spray system.

Table 1. Experimental conditions for TiO_2 coating deposition

Forward power (kW)	0.3, 0.5
Working gas	Ar
Working gas flow rate (l/min)	15
Spray distance (mm)	30, 35, 40
Traverse speed (mm/s)	5
Deposition time (s)	210
Antenna outlet diameter (mm)	2.5

2.1.2 Materials

In this experiment, titanium dioxide, TiO_2 powder which possesses the melting point of 2143 K is used as feedstock powder to deposit coatings. TiO_2 powder (ATP100-ϕ15μm, KOJUNDOKAGAKU Research Centre) has the average size of 15 μm with the anatase content rate of above 96%. SEM image of TiO_2 powder is shown in Figure 2. The substrate material used in this research is SUS304. As the pre-treatment for the substrates before spraying, the surface of the substrates was grit blasted and then cleaned by ethanol. Size for both kinds of substrates was set at the dimension of 20 mm x 20 mm x 3 mm.

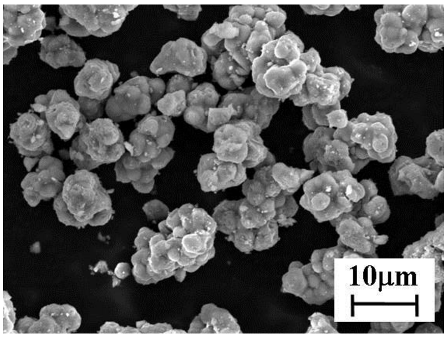

Figure 2. SEM image of TiO_2 particles.

2.2 Evaluation methods

Observation of coating surface and cross section was conducted using scanning electron microscope (SEM: JSM-6390TY, JEOL Co. Ltd.). The measurement of the porosity inside the coating was conducted by using the digital image analysis (imageJ software) on the coatings cross sectional morphologies. The area percentage of porosity was calculated from the binary images of the cross-sectional morphologies. Substrate temperature was measured at the position of 1.0 mm from the surface of the substrate by K-type thermocouple. The phase composition in the deposited coatings was verified by X-ray diffraction analysis (XRD: RINT-2500, Rigaku), with CuK_α radiation. The operating conditions were 30 kV and 80 mA for particles and 160 mA for the coatings respectively. The goniometer was set at a scan rate of 4 °/min at the range of $20° \leqq 2\theta \leqq 90°$. The anatase content rate in the coatings was estimated based on the following equation developed by Berger-Keller et al. [8]:

$$A = \frac{1}{1 + 1.265\frac{I_R}{I_A}} \times 100 \tag{1}$$

I_A : Intensity of anatase phase (101), I_R : Intensity of rutile phase (110)

2.3 Investigation of the influence to the anatase content rate by the change of substrate temperature

This evaluation has been done in order to investigate the influence of substrate temperature to the anatase content rate. During the solidification of titanium dioxide, the nucleation and growth of the rutile phase is formed by usual coagulation process. However, in the case of rapid cooling rate of higher than 1.0×10^6K/s, rather than forming the rutile phase, the anatase phase is generated selectively [9, 10]. This experiment is conducted in order to clarify the influence of substrate temperature to the anatase content rate. The substrates were heated on the hot plate on the atmospheric condition and the temperature was set to 473, 573 and 673 K.

2.4 Investigation of the anatase phase occurrence by using heat-treated powder

The generation of anatase phase during the experimentation and the anatase content rate was investigated and evaluated. In order to clarify the rapid cooling rate effect towards the nucleation of anatase phase, the powder particles with the rutile content rate of 99 % were used. The 96% pure anatase phase particles powder was heat treated by using heat furnace. Heat treatment was conducted in low pressure condition with nitrogen environment and the time was set for 30 min. Since the temperature for the phase transformation is 1127 K, the setup temperature for the heat furnace was set at 1223 K to be slightly higher to ensure the phase change to be occurred significantly. After the heat treatment, since some of the particles were observed to be agglomerated, sieve with mesh size of 38 μm was used to distribute the powder to smaller size. Figure 3 shows the SEM images and the XRD patterns of the powder particles before and after the heat treatment. Heat treated particles were changed to 99% of rutile content rate after the treatment. Spray distance of 40 mm and different input power of 0.3 and 0.5 kW were set as spray conditions due to the highest possession of anatase content rate in the coating deposition. The coatings deposited by using the heat treated particles were analysed by XRD and the anatase content rate was calculated.

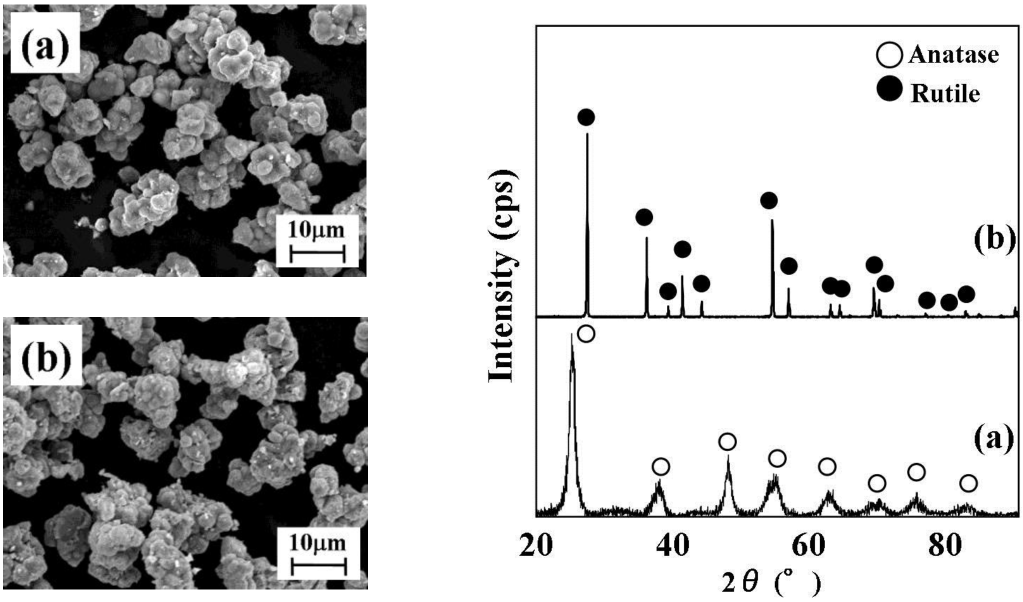

Figure 3. Photograph and XRD patterns of (a) before heat treatment (b) after heat treatment

2.5 Anatase content rate investigation of in-flight particles

In this study, the change of anatase content rate of the particles during flight was investigated. This is to investigate the mechanisms of anatase phase formation of particles during flight without the effect of substrate temperature. The particles were collected at spray distance of 200 mm. The evaluation was conducted to both heat treated and non-treated powder particles with the anatase content rate of 96 % and 0.02 % respectively.

3. Results and Discussion

3.1 Deposition of TiO_2 coating

Figure 4 and 5 show the SEM images of cross sectional morphology of TiO_2 coating deposited under 0.3 kW and 0.5 kW of input power and the enlarged images respectively. Meanwhile, coating porosity analysis of the coating is shown in Figure 6. From the result in Figure 4, it can be observed that there is no influence of spray distance to the coating thickness where the thickness is approximately 10 μm irrespective of any spray distance. It is also the same with the appearance porosity that can be observed from the enlarged morphologies in which the spray distance do not contributes much towards the coating porosity and the results of coating porosity analysis also recorded the same. Meanwhile, at 0.5 kW as shown in Figure 5, the coating deposition differs much in this spray condition in which the porosity inside the coating is observed to be lower with the decrease of spray distance. At the lowest spray distance of 30 mm, dense coating of approximately 200 μm is able to be fabricated. From the comparison of the coating deposited on 0.3 kW and 0.5 kW, the porosity of the coating is higher in the former. At spray distance of 40 mm, it can be observed that almost same coating thickness was obtained by both input power conditions. On the other hand, at spray distance of 30 and 35 mm, the coating thickness increased with the increase of input power from 0.3 kW to 0.5 kW. This is due to the elongation of plasma length caused by the increase of input power which results in the increase of the dwelling time of particles inside the plasma plume [11]. From this, sufficient melting is occurred while impacting the surface of the substrate as a result of the increase of energy given from the plasma.

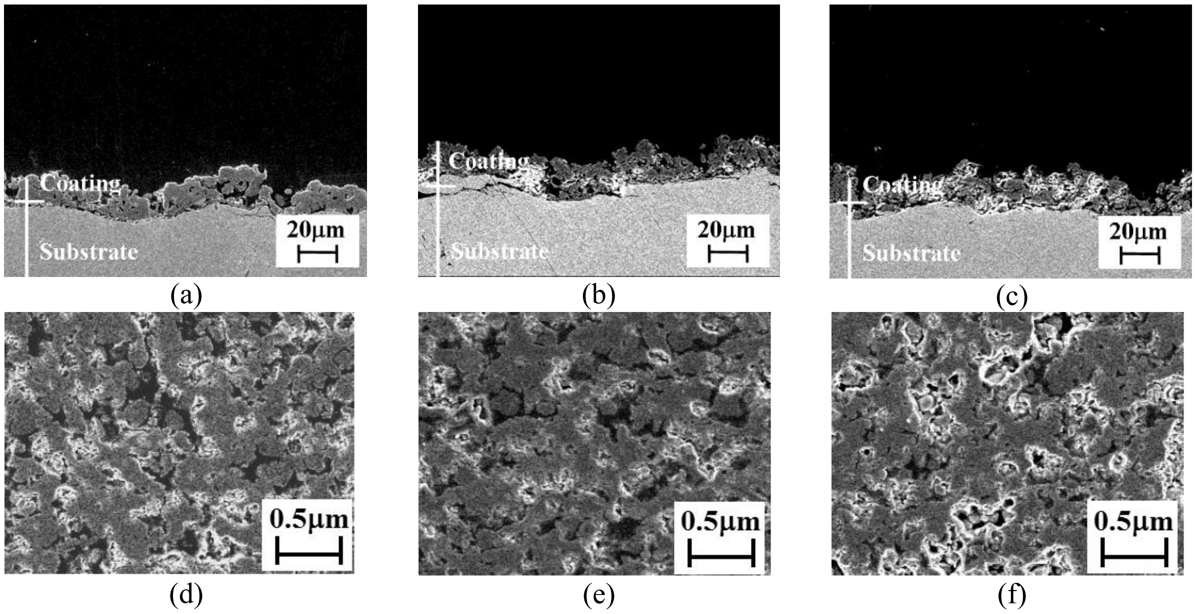

Figure 4. Cross sectional SEM images of TiO_2 coating at 0.3 kW with spray distance of (a) 30 mm, (b) 35 mm, (c) 40 mm and (d), (e), (f) are the magnified view of (a), (b), (c) respectively.

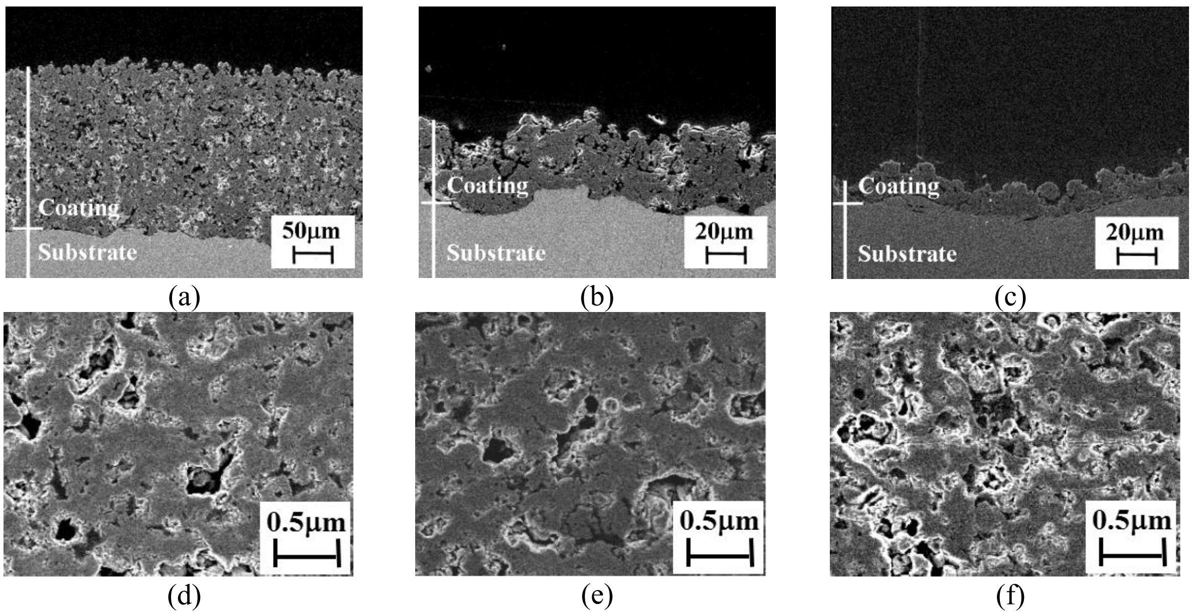

Figure 5. Cross sectional SEM image of TiO_2 coating at 0.5 kW with spray distance of (a) 30 mm, (b) 35 mm, (c) 40 mm and (d), (e), (f) are the magnified view of (a), (b), (c) respectively.

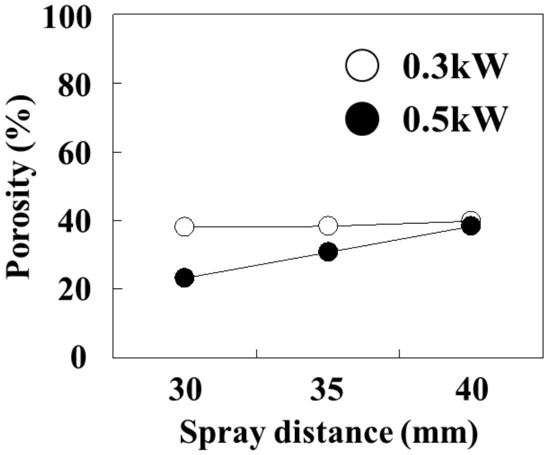

Figure 6. Porosity of the coatings at 0.3 kW and 0.5 kW of input power with the change of spray distance.

Figure 8 shows the correlation of substrate temperature with input power and spray distance. The substrate temperature decreased with the increase of spray distance and irrespective of input power. At a constant spray distance, the substrate temperature was lower with input power of 0.3 kW compared to that of 0.5 kW. This is due to the reduction of the plasma length resulting from higher working gas flow rate. An increase in working gas flow rate induced the reduction of the energy given per unit working gas volume at constant microwave energy, resulting in decrease in plasma length because of the thermal pinching effect [12].

Figure 9 shows the graph of anatase content rate by the change of input power calculated from the results obtained by the XRD analysis. From the results, anatase content rate shows the tendency of increase with the increase of spray distance irrespective of input power conditions. Furthermore, the anatase content rate increases significantly from the lowering of input power and the maximum rate is recorded at spray distance of 40 mm and input power of 0.3 kW. From the decrease of input power from 0.5 kW to 0.3 kW, it is known that due to the decrease of dwelling time of particles inside the plasma, the controlling factor of heat input towards the particles is obtained.

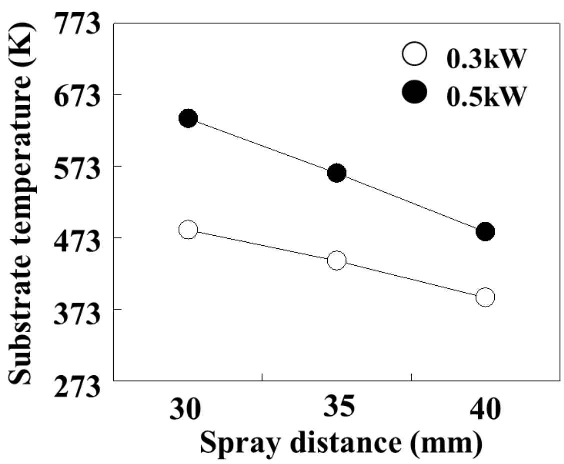

Figure 7. Correlation of substrate temperature with input power and spray distance.

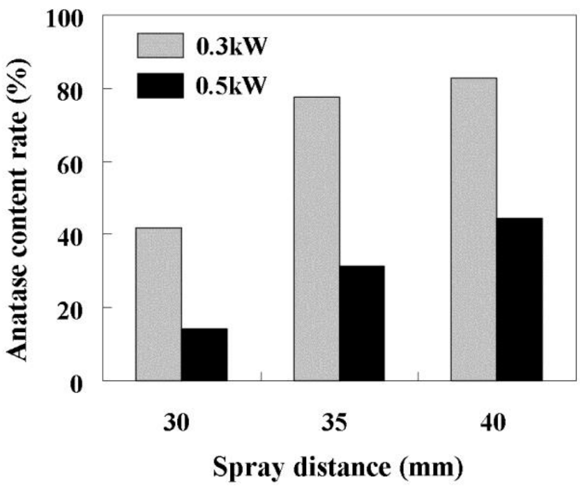

Figure 8. Anatase content rate of TiO_2 coating by the change of input power and spray distance.

3.2 Effect of substrate temperature to the anatase content rate

Figure 9 shows the XRD results of the coating deposited on 473 K, 573 K, and 673 K of preheated substrate temperature at 0.3 kW and 0.5 kW of input power. It can be seen that the intensity peak of rutile phase decreased while the peak of rutile phase is increased by the increase of spray distance irrespective of input power conditions. Table 2 shows the results of calculated anatase content rate of the deposited coatings by the change of substrate temperature in compare to non-preheated substrate. From the result, it is known that the anatase content rate is decreased with the increase of substrate temperature in the preheated specimens. At input power of 0.5 kW and spray distance of 40 mm, the non-preheated substrate temperature is 481 K, the anatase content rate of the deposited coating is 43 % while the anatase content rate of preheated at 673 K is 34 %. This shows that the anatase content rate decreased with the increase of substrate temperature. This value is further elevated and became significant in the case of the coatings deposited at input power of 0.3 kW. From the results, it is clarified that by lowering the substrate temperature, the deposition of TiO_2 coatings with higher anatase content rate is possible.

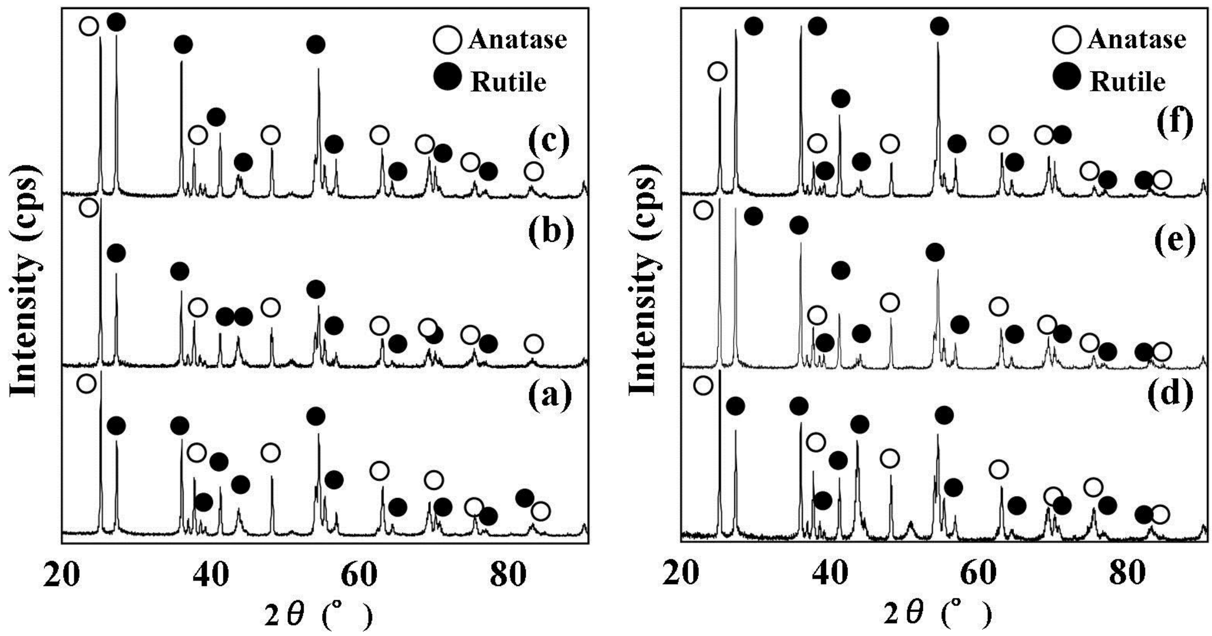

Figure 9. XRD results of coatings deposited at input power of (a)-(c) 0.3 kW, (d)-(f) 0.5 kW and preheated substrate temperature of (a),(d) 473 K, (b),(e) 573 K and (c),(f) 673 K

Table 2. Anatase content rate (%) of TiO_2 coating at different substrate temperature

		Input power (kW)	
		0.3	0.5
Without substrate heat (Substrate temperature (K))		83 (389)	43 (481)
Substrate temperature (K)	473	58	41
	573	58	39
	673	53	34

3.3 Effect of powder heat treatment to the anatase content rate

Figure 10 shows the XRD patterns of the coatings deposited by using heat treated particles at input power of 0.3 kW and 0.5 kW. From the results, it can be seen that the intensity peak of anatase phase is generated irrespective of input power profile and the tendency of the increase of anatase phase peak with the lower input power is observed. The heat treated particles were only consist of the rutile phase before the spray as shown in Figure 3, while after the spray, the occurrence of anatase phase is observed means that the phase change were occurred during spray. Table 3 shows the anatase content rate of deposited TiO_2 coatings by using heat treated particles at before and after sprayed at 0.3 and 0.5 kW of input power. It is clarified that the anatase content rate increased after spray irrespective of input power conditions while 0.3 kW shows higher value than 0.5 kW. This is due to the fact that the substrate temperature is lower at input power of 0.3 kW at spray distance 0f 40 mm which recorded 389 K in compare to 481 K in the counterpart. The lowering of the substrate temperature promotes higher cooling rate and this increases the anatase content rate inside the coatings. Moreover, the anatase content rate of the coatings deposited by heat treated particles shows significant decrease in compare to the non-treated ones. Therefore, it is considered that most of the molten particles which travelled inside the plasma plume were not nucleated to rutile phase during spray. Due to the above reasons which including the high porosity (above 40 %), coatings by the non-treated particles are mostly consist of insufficient melting condition which results in the coatings with mainly anatase phase.

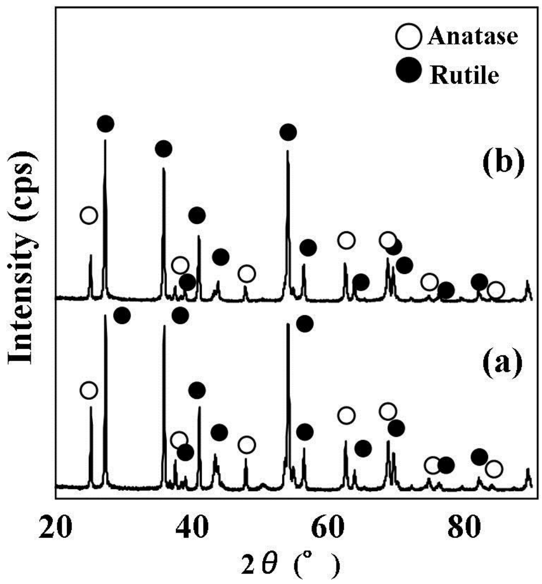

Figure 10. XRD patterns of TiO_2 coatings at input power of (a) 0.3kW, (b) 0.5kW

Table 3. Anatase content rate (%) of deposited TiO_2 coatings by using heat treated particles at before and after spray at different input power

	Before spray	After sprayed at input power (kW)	
	Rutile rich TiO_2 particles	0.3	0.5
Anatase content rate (%)	0.02	27.4	18.6

3.4 Investigation of anatase content rate of in-flight particles

Figure 11 shows the XRD results of the non-treated particles at different input power. From the results, it is clarified that by lower input power of 0.3 kW, the intensity peak of anatase phase is increased. This is attributed to the increase of heat input per unit power which resulting in increasing number of molten particles during spray. Therefore, it is considered that most of the molten particles which travel inside the plasma are mainly nucleated to rutile phase.

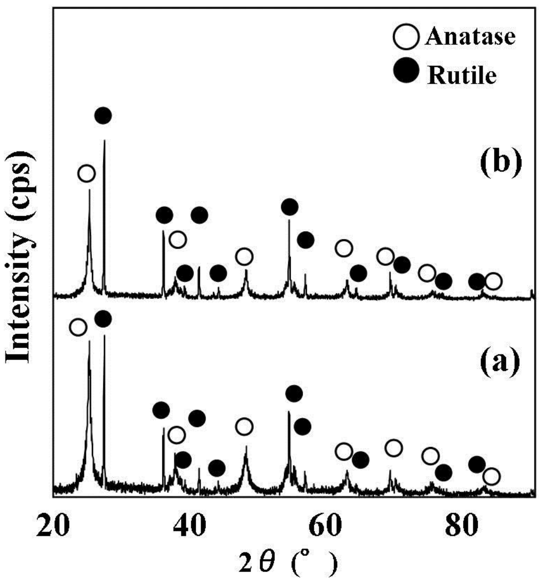

Figure 11. XRD patterns of TiO_2 coatings by using non-treated particles at input power of (a) 0.3kW, (b) 0.5kW

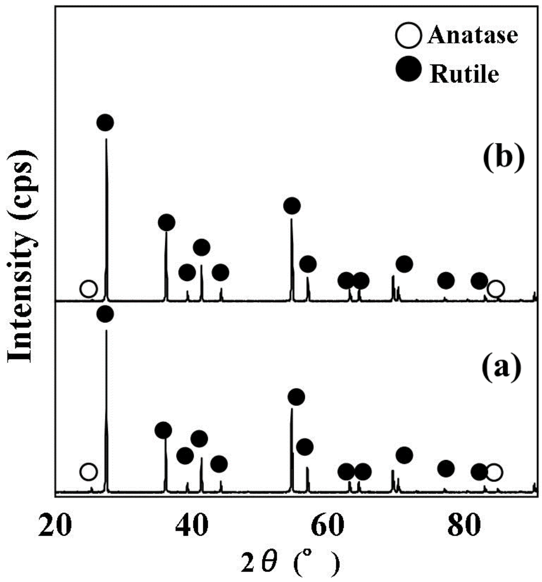

Figure 12. XRD patterns of TiO_2 coatings by using heat treated particles at input power of (a) 0.3kW, (b) 0.5kW

Table 4. Anatase content rate (%) of in-flight non-treated and heat treated particles at different input power

	Particles type	
	Non-treated	Heat treated
0.3kW	43.3	2.3
0.5kW	35.3	0.7

Figure 12 shows the X-ray diffraction results of the heat treated particles at different input power. It is known from the results that the rutile phase of the collected particles is high. However, the peak of anatase phase which is not existed before spray can be observed irrespective of any input power conditions. By lowering the input power, the intensity peak of anatase phase is increased. The calculated anatase content rate from the XRD results is shown in Table 4. From this, it is already known that some of the melted particles are solidified during flight resulting in the phase transformation. However, on the same condition as the collected particles, the anatase content rate are higher in the deposited coatings on substrates is to be inferred as mainly the effect of cooling occurred on the surface of the substrate as the generation of the anatase phase nucleation.

4. Conclusions

The summary of the things that had been clarified from the study of the deposition of titanium dioxide coating by low power atmospheric pressure microwave plasma spray and the characteristics evaluation are listed below.

1. The deposition of titanium dioxide coating onto SUS304 is possible by using low power atmospheric pressure microwave plasma spray at input power of 0.3 and 0.5 kW.
2. The anatase content rate of the titanium dioxide coating increased with the reduction of the input power and by the increment of spray distance. The highest anatase content rate of 83 % is recorded at the spray condition of input power 0.3 kW and at spray distance of 40 mm.
3. From the coating deposited by 99 % of rutile content rate titanium dioxide powder, the anatase content rate increased inside the as-sprayed coating proved that the nucleation of anatase phase occurred during the spray.
4. The anatase content rate inside the as-sprayed coating is increased with the decrease of substrate temperature.

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