Plasma-spraying synthesis of high-performance photocatalytic TiO₂ coatings

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Abstract. Anatase (A-) TiO₂ is a photocatalytic material that can decompose air-pollutants, acetaldehyde, bacteria, and so on. In this study, three kinds of powder (A-TiO₂ without HAp, TiO₂ + 10mass%HAp, and TiO₂+30mass%HAp, where HAp is hydroxyapatite and PBS is polybutylene succinate) were plasma sprayed on biodegradable PBS substrates. HAp powder was mixed with A-TiO₂ powder by spray granulation in order to facilitate adsorption of acetaldehyde and bacteria. The crystal structure was almost completely maintained during the plasma spray process. HAp enhanced the decomposition of acetaldehyde and bacteria by promoting adsorption. A 10mass% HAp content was the most effective for decomposing acetaldehyde when plasma preheating of the PBS was not carried out before the plasma spraying. The plasma preheating of PBS increased the yield rate of the spray process and facilitated the decomposition of acetaldehyde by A-TiO₂ coatings without HAp. HAp addition improved photocatalytic sterilization when plasma preheating of the PBS was performed.

1. Introduction
Anatase titanium dioxide (A-TiO₂) is widely known as a photocatalytic material [1]. Photocatalytic A-TiO₂ coatings help ultraviolet rays decompose toxic substances such as acetaldehyde and sterilize bacteria. The plasma spraying of A-TiO₂ powder is often used to fabricate these materials, but A-TiO₂ transforms to rutile (R-) TiO₂ at temperatures higher than 1188 K [2]. Therefore, the spraying conditions should be controlled so that the A-TiO₂ phase cannot transform into the R-TiO₂ phase during plasma spraying. PBS (polybutylene succinate) plastic is a better substrate for this procedure than metals with high melting points, because the melting point of PBS is 387 K, and so PBS can adhere to A-TiO₂ more easily than metals at low temperatures (with low heat-input). In other words, it is very easy to obtain A-TiO₂ coatings on PBS by plasma spraying, and it is possible to retain the A-TiO₂ structure after spraying [2, 3]. PBS is a biodegradable plastic, and TiO₂ is harmless. Therefore, it is environmentally friendly to make photocatalytic A-TiO₂ coatings on PBS. HAp (hydroxyapatite) adsorbs acetaldehyde, mold, and bacteria. Thus, A-TiO₂ powder mixed with HAp powder can enhance the decomposition rate. It is therefore important to investigate the plasma-spraying synthesis of A-TiO₂ coatings mixed with HAp powder and to examine the photocatalytic properties of the resulting materials [4]. The purpose of the present study is to synthesize high-performance photocatalytic A-TiO₂ coatings by plasma spraying and to verify the effect of HAp on the photocatalysis.
2. Experimental procedure
The size (coating area) of the PBS substrate for plasma spraying was 50 mm × 50 mm, and the thickness was 9 mm. The three kinds of spraying materials were A-TiO₂ powder, A-TiO₂ + 10mass%HAp powder (TiO₂+10%HAp), and A-TiO₂ + 30mass%HAp (TiO₂+30%HAp) powder. The mixed powder was made by spray granulation. The average diameters of the A-TiO₂ and HAp powders before spray-granulating were 200 nm and 5 µm, respectively. The plasma spraying conditions are shown in Table 1. Figure 1 shows a cross sectional illustration of the plasma torch used in this study. The plasma spraying was carried out either without preheating the PBS or immediately after preheating. The preheating of PBS was performed in a one-pass traverse to increase the yield rate of the sprayed coatings and to increase the anatase ratio (abundance fraction of the A-TiO₂ phase). The preheating was carried out under an arc current of 300 A to increase the coating yield rate. The traverse speed was 50 mm/s. The coatings were observed with a scanning electron microscope (SEM). The coating structures were measured by X ray diffraction (XRD). The anatase ratio \( f \) (parentage fraction) in the coatings is determined by

\[
 f = \frac{1}{1 + 1.265 \frac{I_R}{I_A}} \times 100 \tag{1}
\]

where \( I_A \) and \( I_R \) are, respectively, the maximum peak values of A-TiO₂ and R-TiO₂ in the XRD graphs [5]. The photocatalytic properties of the materials were investigated by examining the decomposition (or sterilization) of acetaldehyde or bacteria (Staphylococcus aureus: IFO 12732). For investigations of the decomposition of acetaldehyde, air (temperature: 25°C; humidity: 50%; volume: 2×10⁻³ m³) containing 100 ppm acetaldehyde was prepared in a glass vessel (flask) in which a specimen with a coated area of 2500 mm² was hung, as shown in Figure 2. Ultraviolet light with a peak wavelength of 352 nm was applied at 20 W to the specimen from the bottom of the flask. The distance between the coatings and the light source was 10 mm. The amount of acetaldehyde remaining was measured by a gas detector after the designated irradiation time \( t \). On the other hand, for the estimation of the sterilizing power, a loopful of inoculum (S. aureus) was put into 150 cm³ of the 100 % NB (nutrient broth) medium and the fungus liquid (solution) was cultivated for 20 hours at 37°C. Then, 1 cm³ of the fungus liquid was diluted to 0.5% in 200 cm³ of the NB medium to obtain the testing solution (10⁵ cfu[colony forming units]/cm³), as shown in Figure 3. For each experiment, 200 cm³ of the testing solution was poured into a glass flask and the coated specimen was hung (dipped) into the solution, as shown in Figure 4. The sample was irradiated with ultraviolet light (black light) with a peak

| Parameters (unit) | Values | Non-preheating | With preheating |
|------------------|--------|----------------|-----------------|
| Ar pressure (MPa) |        | 0.48           | 0.41            |
| Distance between gun and substrate (mm) | 100 | 100            |
| Arc current (A) |        | 500            | 300             |
| Traverse speed (mm/s) | 165 | 50             |
| Stepping width (mm) | 4.0 | 5.0            |
| Spraying pass |        | 2              | 2               |

Table 1. Preheating and plasma spraying conditions.
Figure 1. Schematic diagram (cross section) of plasma spray torch.

Figure 2. Experimental method for photocatalytic acetaldehyde decomposition.
Figure 3. Preparation of fungus liquid from inoculum (S. aureus).

Figure 4. Experimental method for photocatalytic sterilization of S. aureus.
wavelength of 352 nm at 20 W from a distance of 10 mm for the designated irradiation time \( t \). The total viable bacterial count \( C \) per unit cm\(^3\) \((C_0 \text{ at } t = 0 \text{ s})\) was measured using the spread plate method (incubation conditions: 37°C, humidity > 90%, 48 hours) to estimate the sterilizing ability of the material. The spread plate method is illustrated in Figure 5. The bacteria-adsorption characteristics of HAp were also estimated by using fungus liquid with a concentration of 10\(^6\) cfu/cm\(^3\). In these experiments, 3 cm\(^3\) of the fungus liquid was poured into a test tube, and a specimen with a coated area of 400 mm\(^2\) was dipped in the fungus liquid and stirred at 70 rpm for 24 hours at 4°C in an atmosphere with 50% humidity without light. After that, the total viable bacterial count was measured in the same way using the spread plate method.

3. Results and discussion

Figure 6 shows the surface morphology and XRD results for the spraying powder after spray granulation. The surface morphologies of the different powders are not so different just after granulation, as seen in Figure 6. The average diameters were about 34 µm. R-TiO\(_2\) peaks are not observed. The TiO\(_2\) powder has no HAp peaks.

Figure 7 shows cross sectional views of the sprayed coatings. The photos in the left column were obtained after plasma spraying without preheating of the PBS, and those in the right column were obtained with preheating of the PBS. As seen in Figure 7, the preheating makes it easier for the sprayed particles to implant into the PBS substrate, since the substrate surface is premelted. This increases the coating yield rate.

Figure 8 shows the surface morphology obtained after spray coating. The surface morphology is not strongly influenced by the preheating or the addition of HAp.
Table 1. Surface morphology and X-ray diffraction patterns of the three kinds of spraying powders.

| Surface morphology | X-ray diffraction |
|--------------------|-------------------|
| TiO₂               | ![TiO₂ XRD](image1) |
| 10%HAp             | ![10%HAp XRD](image2) |
| 30%HAp             | ![30%HAp XRD](image3) |

**Figure 6.** SEM images showing the surface morphology and XRD patterns of the three kinds of spraying powders.

Table 2. Cross-sectional SEM images of sprayed coatings.

| Non-preheated substrate | Preheated substrate |
|-------------------------|---------------------|
| TiO₂ coating            | TiO₂ coating        |
| 10%HAp coating          | 10%HAp coating      |
| 30%HAp coating          | 30%HAp coating      |

**Figure 7.** Cross-sectional SEM images of sprayed coatings.
Figure 8. Surface morphologies (SEM images) of sprayed coatings.

Figure 9. XRD patterns of sprayed coatings with different HAp compositions.
Figure 9 shows the XRD results for the coating plasma sprayed without preheating. The R-TiO₂ peaks are very small, and a small HAp peak was also observed when HAp was mixed with A-TiO₂. The anatase ratio of each coating is greater than 94%, as shown in Table 2. Preheating can increase the anatase ratio.

Table 2. Anatase ratio obtained for different HAp contents with and without preheating.

| Plasma preheating       | TiO₂ | 10%HAp | 30%HAp |
|-------------------------|------|--------|--------|
| Without preheating      | 94.4 | 95.1   | 95.5   |
| With Preheating         | 96.3 | 95.8   | 100    |

Figure 10 shows the changes in acetaldehyde concentration with time for the sprayed coatings fabricated (a) without preheating and (b) with preheating. It is found that the A-TiO₂+10mass%HAp coatings are the most effective for decomposing acetaldehyde without preheating. If the substrate is
Figure 11. Photocatalytic decomposition of acetaldehyde by sprayed coatings with different HAp contents fabricated (a) without preheating and (b) with preheating.

Figure 12. Adsorption ability of HAp.
preheated, A-TiO\textsubscript{2} without HAp shows the highest decomposition rate. This is a very interesting result, but the reason for this phenomenon is not known.

Figure 11 shows the changes in $C/C_0$ with time for sprayed coatings fabricated (a) without preheating and (b) with preheating. HAp has a large effect on the sterilization ability of the coating. In particular, HAp can improve the sterilization performance of the coatings fabricated with preheating, as seen in Figure 11 (b). Figure 12 shows experimental results on the bacteria adsorption function of HAp. The total viable count decreases with increasing HAp content. It is found that HAp improves the photocatalytic properties of A-TiO\textsubscript{2} through its bacteria-adsorption function.

4. Conclusion
Photocatalytic A-TiO\textsubscript{2}–HAp coatings were fabricated by plasma spraying. The acetaldehyde decomposition and sterilization performance of the coatings were then investigated. The main results are as follows:
1) HAp addition is useful for obtaining high-performance photocatalytic TiO\textsubscript{2} coatings fabricated by plasma spraying.
2) Preheating the PBS increases the coating yield rate and the anatase ratio.
3) The sprayed particles are implanted into the PBS by plasma spraying.
4) TiO\textsubscript{2}-10\%HAp coatings are the most effective catalysts for acetaldehyde decomposition.
5) If preheating is carried out, TiO\textsubscript{2} coatings without HAp decompose acetaldehyde very well.
6) HAp improves the photocatalytic sterilization performance of the coating through its bacteria-adsorption function.

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