Formation of Hydroxyapatite/Titania Composite Film with Two Aerosol Beams

Masahiro TSUKAMOTO*, Hitoshi NAKANO** and Nobuyuki ABE*

(Received Jun 7, 2010)

A hydroxyapatite/titania composite (HAp/TiO₂) film was developed for application in air purification and as an antibacterial, antifouling film. This HAp/TiO₂ film has the ability for adsorbing and decomposing organic matter. To obtain the HAp/TiO₂ film, we used two kinds of aerosol beams. They were composed of TiO₂ and HAp particles accelerated by flow of helium gas, respectively. First layer, TiO₂ film, was formed on a glass plate with a TiO₂ aerosol beam. Second layer, HAp film, was created on the first layer, TiO₂ film. Neither the substrate nor HAp and TiO₂ particles were heated during deposition. Acetaldehyde concentration reduced by the HAp/TiO₂ film was measured to evaluate the film's ability for adsorbing and decomposing organic matter.

Key Words: Hydroxyapatite, Titania, Coating Technology, Film Formation, Aerosol Beam, Composite Film, Photocatalyst

1. Introduction

Anatase phase titanium dioxide (TiO₂) is widely used in environmental cleaning because of its photocatalytic properties when it is irradiated with ultraviolet (UV) light (wavelength: $\lambda < 390$ nm), enabling decomposition of organic matter such as bacteria, mold and odors.^{1,2)} Drawback of TiO₂ is that the photocatalytic properties of TiO₂ are not displayed when UV light is absent, such as at night. Therefore, additional function to TiO₂, enabling adsorption of organic matter at night, is required. Hydroxyapatite (HAp: Ca₁₀(PO₄)₆(OH)₂) actively adsorbs organic matter³⁾ without using UV light. However, HAp is not able to decompose it. So its surface becomes saturated with organic matter over time.

A film composed of TiO₂ and HAp, HAp/TiO₂ film, overcomes the respective drawbacks of TiO₂ and HAp by both adsorbing and decomposing organic matter, making it highly suitable for environmental cleaning. In previous study, we developed the hybrid aerosol beam (HAB) deposition method for fabricating one layered HAp/TiO₂ film on the substrate.⁴⁾ TiO₂ and HAp particles were simultaneously ejected from one nozzle in the HAB method. This method is based on coating technology with an aerosol beam.⁵⁻⁸⁾ An aerosol beam is composed of submicron-size particles accelerated by gas flow to velocities of 200 - 650 m/s. When a substrate is irradiated with an aerosol beam, the particles collide with the substrate and form a film. During impact, it is probable that some of the kinetic energy of particles is converted

into thermal energy that promotes bonding between the particles and the substrate. However, the actual bonding mechanism has not yet been elucidated. In aerosol beam coating, neither the particles nor the substrate are heated during deposition, which is advantageous compared with other coating methods that require high temperatures (e.g., thermal spraying and pulsed laser deposition). Therefore, the particles retain their crystal structure during aerosol beam irradiation.

In this study, we proposed that the coating technology using two kinds of aerosol beams, TiO₂ and HAp aerosol beams, was applied to creation of two layered HAp/TiO₂ film, which had two functions of adsorbing and decomposing organic matter. This film was composed of HAp film on TiO₂ film. First layer, TiO₂ film, was formed on a glass plate with a TiO₂ aerosol beam. Second layer, HAp film, was created on the TiO₂ film with a HAp aerosol beam. When HAp film formed on TiO₂ film is dense, organic matter can not reach the TiO₂. Then, organic matter is not decomposed with UV light since the organic matter does not contact the TiO₂ film. When the HAp film is not dense, organic matter can reach the TiO₂ film through the HAp film. Then, organic matter is decomposed through photocatalytic effect by UV light irradiation. Our previous study indicated that the density of HAp film could be controlled with variation of the beam incidence angles. When the plate was irradiated with the beam at an oblique incidence, a force is generated parallel to the surface of the plate in addition to the direction of the normal vector.^{6,8)} This force acting parallel to the surface may push and remove particle

* Joining and Welding Research Institute, Osaka University (11-1, Mihogaoka, Ibaraki, Osaka, 567-0047, Japan)

** Kinki University (3-4-1 Kowakae, Higashi-Osaka, Osaka, 577-8502, Japan)

aggregates with low adhesion that have already been deposited as more particles fly out from the nozzle. At oblique incidence, the HAp film becomes dense since particle aggregates are removed. We investigated the dependence of the beam incident angle on decomposing organic matter. In this experiment, evaluation of the decomposing organic matter with HAp/TiO₂ film and acetaldehyde in the bottle was performed.

2. Experimental

Figure 1 shows a schematic diagram of the aerosol beam processing system for fabricating HAp/TiO₂ film. The film fabrication system with an aerosol beam was primarily composed of an aerosol chamber with a processing chamber connected by a Teflon tube, as shown in **Fig. 1**. Commercial HAp powders (Taihei Chemical Industrial) and TiO₂ powders (Junsei Chemical) were used in our experiments. The HAp particle size was in the 0.1 to 0.5 μm range, although aggregates with a diameter of approximately 1 to 2 μm were formed. The TiO₂ particle size was approximately 0.2 μm . These sizes were confirmed with a scanning electron microscope (SEM). An aerosol was produced by mixing the particles with helium gas using an aerosol vibration system shown in **Fig. 1**. The processing chamber was pumped down with a mechanical booster pump and a rotary pump to produce a pressure difference between the two chambers. Helium gas flowed from the aerosol chamber (0.1 MPa) to the processing chamber (300 Pa). Gas flow rate was 20 L/min. The particles were accelerated by the flow of helium gas and carried to the processing chamber through the Teflon tube and nozzle. The particles ejected from the nozzle impacted with the substrate and were deposited on the substrate surface. The nozzles employed in this experiment had a rectangular orifice of $10.0 \times 0.3 \text{ mm}^2$. The substrates were glass plates with a thickness of 1.3 mm and a surface roughness of approximately 0.02 μm (Ra). The thickness and surface roughness of glass plates were measured with a micrometer caliper and a surface profiler, respectively. The distance between the nozzle and the plate was adjusted to be 5 mm. TiO₂ film with an area of $10.0 \times 20.0 \text{ mm}^2$ on the glass plate was formed by the TiO₂ aerosol beam irradiation with the incident angle of 10°. Thickness of the TiO₂ film was approximately 10 μm . After the TiO₂ film was formed, the TiO₂ film was irradiated with the HAp aerosol beam for creating the HAp film.

The incidence angle of the HAp aerosol beam was varied from 10 to 60° with a period of 10° by rotating the θ stage for HAp film formation. The TiO₂ film position was controlled with an XYZ stage connected to a computer. An area of $10.0 \times 20.0 \text{ mm}^2$ on the surface of the TiO₂ film was scanned by the HAp aerosol beam for 1 minute at room temperature. Neither the TiO₂ film nor the HAp particles was heated during HAp aerosol beam irradiation.

Fig. 1 Schematic diagram of the coating system with two aerosol beams.

Thickness of the HAp film was measured with a surface profiler. Surface morphology of the HAp film was observed with SEM. The HAp/TiO₂ film crystal structure was observed by X-ray diffraction (XRD) analysis.

The decomposition of organic matter on the film was evaluated by temporal variation of the acetaldehyde concentration, which is a conventional method for evaluating the decomposition capacity of TiO₂ film. In this study, this method was applied for continuous evaluation of adsorption by the HAp film and decomposition by the TiO₂ film. First, the TiO₂ or HAp/TiO₂ film was placed in a 1 liter glass container, which was then filled with acetaldehyde adjusted to be an initial concentration of 100 ppm. The acetaldehyde concentration was measured at room temperature with gas detection tubes (No.92M, Gastec Corporation, Japan). The acetaldehyde concentration was then measured every 60 minutes for 180 minutes to determine the HAp's adsorption capacity. At 180 minutes (Starting time of UV light irradiation), the surface of the TiO₂ or HAp/TiO₂ film in the glass container was irradiated with UV light from a black light source to investigate the decomposition capacity of the TiO₂ in the composite film. The film was continuously irradiated for 360 minutes, and the acetaldehyde concentration was measured every 60 minutes.

3. Results and Discussion

Thickness of HAp film formed at incidence angles of 10, 20, 30, 40, 50 and 60° are 15, 13, 9, 7, 6 and 3 μm , respectively. The thickness of the HAp film was decreased from 15 to 3 μm as the beam incidence angle was increased from 10 to 60°. The SEM images of the surface of the HAp films produced with the aerosol beam at incidence angles of 10, 20, 30, 40, 50 and 60° are shown in **Figs. 2(a), (b), (c), (d), (e) and (f)**, respectively. As the images show, the surface morphology was changed as the incidence angle increased. HAp particle shape was observed in **Figs. 2(a), (b), (c) and (d)**. These results suggest that these HAp films at 10, 20, 30

Fig. 2 Surface images of HAp films produced at incidence angles of (a) 10, (b) 20, (c) 30, (d) 40, (e) 50 and (f) 60°.

and 40° were not dense. In Figs. 2(e) and (f), HAp particle shape was not observed. These results suggest that HAp films at 50 and 60° were dense. The XRD patterns of HAp/TiO₂ films formed at 10, 20, 30, 40, 50 and 60° are shown in Figs. 3(a), (b), (c), (d), (e) and (f), respectively. As the patterns show, the crystallinity of HAp was retained throughout the beam irradiation.

Figure 4 shows the acetaldehyde concentration as a function of time. In the 0 to 180 min range, TiO₂ and HAp/TiO₂ films were not irradiated with UV light. For TiO₂ film, no reduction of the acetaldehyde concentration occurred in 180 minutes. For HAp/TiO₂ films, the acetaldehyde concentration was decreased from 100 to 80 ppm in 180 minutes. These results indicate that HAp film of the HAp/TiO₂ film adsorbed the acetaldehyde. After UV light irradiation on the films was started, the acetaldehyde concentration was decreased as the irradiation time increased. For TiO₂ film, the acetaldehyde concentration was decreased from 100 to approximately 0 ppm for 360 min. For HAp/TiO₂ films at 10, 20, 30 and 40°, the concentrations were decreased for 360 min from 80 to 10, 15, 20 and 25 ppm, respectively. These reductions of the acetaldehyde concentration indicate that the acetaldehyde

Fig. 3 XRD patterns of HAp/TiO₂ films formed at incidence angles of (a) 10, (b) 20, (c) 30, (d) 40, (e) 50 and (f) 60°.

Fig. 4 Acetaldehyde concentrations as a function of time.

contacted the TiO₂ films through those HAp films. Reduction rate of the acetaldehyde concentration for 10° was highest in those for 20, 30 and 40°. These results suggests that density of the HAp film at 10° was lowest in another films' densities. For HAp/TiO₂ films at 50 and 60°, the concentration was varied from 80 to 35

and 40 ppm, respectively. This result suggested that the HAp film of HAp/TiO₂ film at 50 and 60° had small holes through which the acetaldehyde reached the TiO₂ film although it might be dense as shown in **Fig. 2(f)**.

4. Conclusions

HAp/TiO₂ films were successfully formed with two kinds of aerosol beam. The XRD pattern of the HAp/TiO₂ film formed at incident HAp aerosol beam angles of 10, 20, 30, 40, 50 and 60° indicated that anatase phase TiO₂ and the HAp structure were retained over the process. HAp film of the TiO₂/HAp film adsorbed acetaldehyde. The TiO₂/HAp films decompose acetaldehyde although the TiO₂ film was coated with the HAp film. Decomposition rate of the TiO₂/HAp film produced at 10° was higher than those produced at 20, 30, 40, 50 and 60°.

Reference

- 1) A. Fujishima and K. Honda: Bull. Chem. Soc. Jpn., 44 (1971) 1148 - 1150.
- 2) A. Fujishima and K. Honda: Nature, 238 (1972) 37 - 38.
- 3) A. Tiselius, S. Hjertén and Ö. Levin: Arch. Biochem. Biophys., 65 (1956) 132 - 155.
- 4) T. Fujihara, M. Tsukamoto N. Abe, S. Miyake, T. Ohji and J. Akedo: Trans. Mater. Res. Soc. Jpn., 30 (2005) 1017 - 1020.
- 5) J. Akedo, M. Ichiki, K. Kikuchi and R. Maeda: Sens. Actuators A, 69 (1998) 106 - 112.
- 6) M. Tsukamoto, T. Fujihara, N. Abe, S. Miyake, M. Katto, T. Nakayama and J. Akedo: Jpn. J. Appl. Phys., 42 (2003) L120 - L122.
- 7) T. Fujihara, M. Tsukamoto N. Abe, S. Miyake, T. Ohji and J. Akedo: Vacuum, 73 (2004) 629 - 633.
- 8) M. Tsukamoto, N. Nakamura, A. Kitajima, J. Morimoto, N. Abe, J. Akedo: Jpn. J. Appl. Phys., 45 (2006) 7840 - 7844.