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Deposition of Hydroxyapatite Film on Titanium by Ultra-fine Particle Beam†

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Abstract

A hydroxyapatite (HA) film was fabricated on a titanium (Ti) plate by an aerosol deposition method (ADM) using an HA submicron-size particle beam. In this process, neither substrate nor HA particles were heated during deposition. The effect of varying the beam incident angle on the HA film formation was investigated. The incidence angle of the beam was varied from 0° to 60° with a period of 20° by rotation of the substrate. Adhesion strength between the HA film and the Ti plate was increased as the incident angle increased although its thickness was decreased. In the films formed at an incident angle of 60°, the adhesion strength was found to be higher than 30 MPa. Possible formation mechanisms of the HA film dependent on the incident angle were discussed

KEY WORDS: (Hydroxyapatite), (Biomaterial), (Coating Technology), (Aerosol Deposition Method)

1. Introduction

Hydroxyapatite (HA) has good biocompatibility and has been widely used in dentistry and orthopaedics. However it is difficult to use HA as an implant for bone substitution because it has much lower mechanical reliability and workability than such conventional biomaterials as titanium (Ti) and the titanium alloy Ti-6Al-4V[1,2]. A material that combines the mechanical properties of such metals and the bioactivity of HA could be used in implants. An HA film formation with strong cohesive strength, good adhesion to the substrate, retaining crystal structure and high chemical purity is required. Various deposition methods for forming an HA film on Ti and Ti-based substrates have been reported, including plasma spraying[3], ion-beam sputtering[4], ion-beam assisted deposition[5], and pulsed laser deposition[6].

We apply an aerosol deposition method (ADM) using a submicron-size particle beam for the HA film fabrication. The ADM is based on the gas deposition method[7] (GDM) and it has already been effectively applied to the formation of lead-zirconate-titanate (PZT) films[8]. When a Ti substrate is irradiated with the beam, the HA particles collide with the substrate and form a film. It is probable that some of the particles' kinetic energy is converted during impact into thermal energy that promotes bonding between the particles and substrate. However, the actual bonding mechanism has not yet been elucidated. In the ADM, neither the particles nor the substrate are heated during deposition, which is advantageous compared to other coating methods that require high temperatures. For example, the particles can retain their crystal structure during and after the process. In the first stage of this study to produce an HA film on Ti plates by the ADM, we investigated the effect of

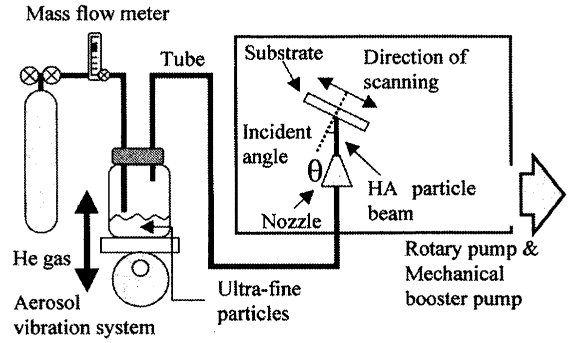

Fig. 1 Schematic diagram of film fabrication system by aerosol deposition method.

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Table. 1 Experimental condition.

Pressure difference between the two chambers	1 atm
Orifice size of nozzle	6 mm x 0.3 mm
Roughness of Ti plate	0.04 μm
Distance between the nozzle and substrate	10 mm
Beam incident angle	0° 20° 40° 60°
Scanning area	6 mm x 5 mm
Beam irradiation time	1 min

varying the beam's incident angle on the surface, cross section, thickness and adhesion strength of the HA film produced. The crystallinity was also evaluated.

2. Experimental Procedure

The HA film fabrication system by ADM was primarily composed of an aerosol chamber and a processing chamber connected by a tube, as 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. An aerosol was produced by mixing the HA particles with Helium (He) gas using a vibration system. He gas flowed from the aerosol chamber to the processing chamber. The HA particles were accelerated by the flow of He gas and carried to the processing chamber through the tube and nozzle. The HA particles ejected from the nozzle impacted with the substrate and were deposited on the substrate's surface.

The experimental conditions are presented in **Table 1**. During the experiments the pressure difference between the two chambers was 1 atm. The nozzle employed in this experiment had a rectangular orifice of 6 x 0.3 mm in size. The substrates were Ti plates polished to a roughness (Ra) of around 0.04 μm. The distance between the nozzle and the Ti plate was 10 mm. The incident angle of the beam was varied from 0° to 60° with a period of 20° by rotation of the θ stage. The beam scanned an area of 6 × 5 mm on the Ti plate for 1 min at room temperature. The Ti plate and the HA particles were not heated during the coating process. The HA particles' size was in the 0.1 to 0.5 μm range, although aggregates with a diameter of approximately 1 to 2 μm were formed. In the aerosol chamber in Fig. 1, there were particle aggregates with a diameter of 1 to 2 μm and dispersed submicron-size particles. The particle aggregates could also be accelerated by the gas flow and ejected from the nozzle. The particle cohesion of the aggregates was modified with a ball mill prior to the experiments.

The HA films were formed on the glass plates to observe their cross section. Cross sections of the HA films were obtained by cleaving the glass plates. HA films' surfaces and cross sections were observed with a scanning electron microscope (SEM). The thickness of the HA films were measured with a surface profiler. The adhesion strength was estimated using a tensile testing machine by attaching a titanium rod with a diameter of 5 mm to the HA film with epoxy resin. It was pulled with a loading rate of 0.2 mm/min until failure of the HA film. The film's crystal structure was observed by X-ray diffraction (XRD).

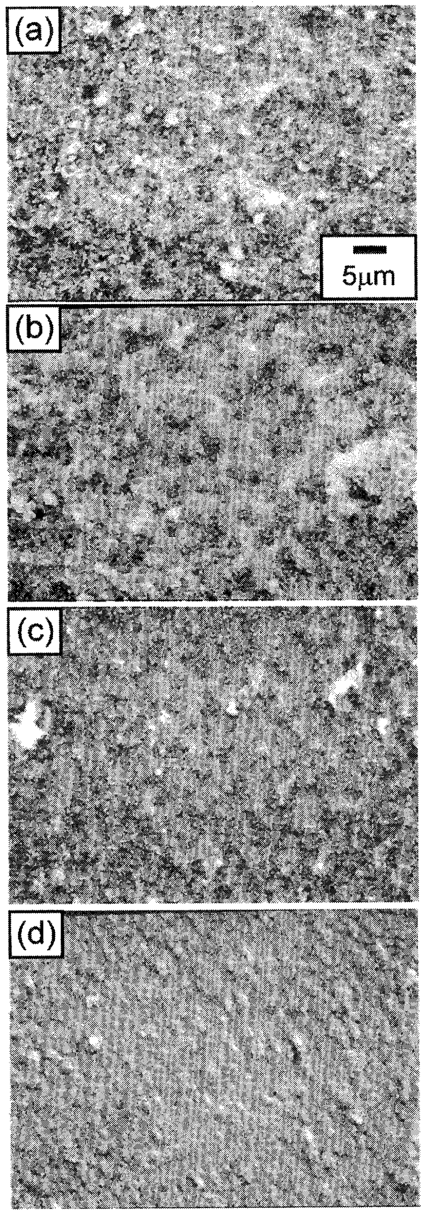

Fig. 2 HA film surfaces observed with a SEM for incident beam angles of (a) 0°, (b) 20°, (c) 40° and (d) 60°.

3. Results and Discussion

The surfaces of the HA films produced at incident angles of 0°, 20°, 40° and 60° as observed with a SEM are shown in **Figs. 2 (a), 2 (b), 2 (c) and 2 (d)**, respectively. As the images show, the roughness of the surface was modified as the incident angle increased. **Figure 3** shows the cross-section images of the HA films formed at

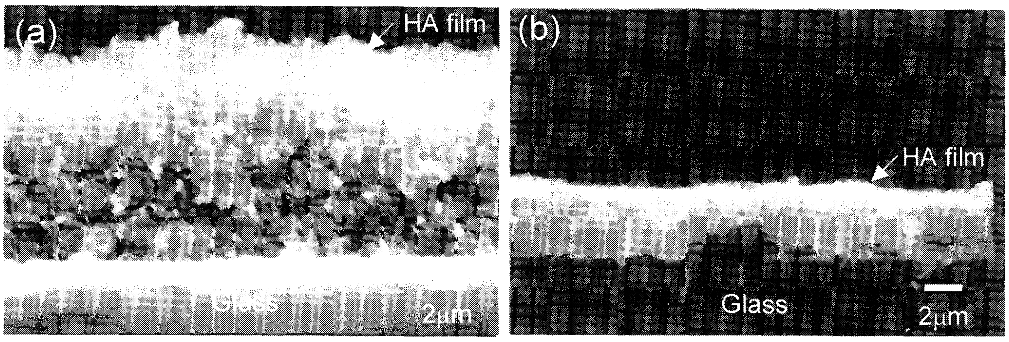

Fig. 3 SEM images of cross sectional view of HA film formed at (a) 0° and (b) 60°.

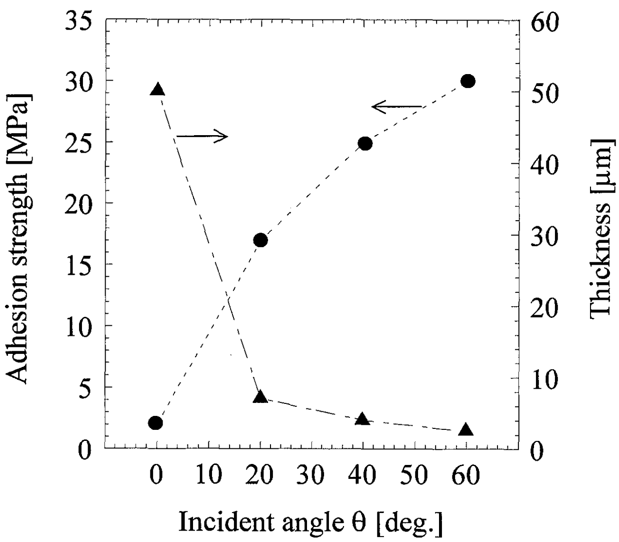

Fig. 4 Adhesion strength(●) and thickness(▲) of the HA film formed on the Ti plate as a function of incident angle.

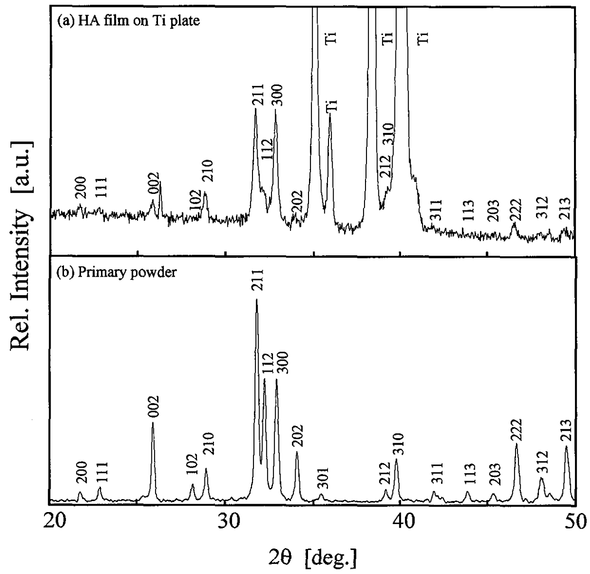

Fig. 5 X-ray diffraction patterns of (a) HA film on Ti plate and (b) primary powder.

incident angles of (a) 0° and (b) 60° on the glass plate. As shown in Figs. 3 (a) and 3 (b), the particle shape was observed for 0°, but it was not observed for 60°. **Figure 4** shows the thickness and the adhesion strength of the HA film formed on the Ti plate as a function of incident angle. The thickness of the HA film was a maximum (50 μm) for 0°, and decreased to 2.5 μm as the angle was increased to 60°. With increasing the incident angle, the thickness of the HA film decreased. Adhesion strengths of the HA film formed at incident angles of 0°, 20°, and 40° were determined to be 2, 17 and 25 MPa on the Ti plate, respectively. Increasing the incident angle led to an increase of the adhesion strength. In the tensile test of the films formed at 60°, the epoxy resin layer bonding the HA film to the titanium rod broke before the films failed. Although the absolute values could not be measured, the films' adhesion strength is assumed to be higher than 30 MPa, since the adhesion strength between the epoxy resin layer and titanium rod was determined to be 30 MPa.

There were particle aggregates with a diameter of 1 to 2 μm and dispersed submicron-size particles in the aerosol chamber in Fig. 1. The particle aggregates could also be accelerated by the gas flow and ejected from the nozzle. When they impacted with the Ti plate at an incident angle of 0°, they adhered to the substrate as Fig. 2 (a) suggests. However, the adhesion strength was low since the aggregate size was 1 to 2 μm. As described earlier, the adhesion mechanism is possibly the result of the localized thermal energy produced by submicron-size particles impacting at a speed of several hundred meters per second[8]. When particle aggregates impact with other particle aggregates already deposited on the Ti plate, the bonding strength will be reduced. This could explain why the HA film formed at 0° had low adhesion and cohesive strengths. Particle aggregates may also be deposited on the Ti plate at an oblique incidence as suggested in Fig. 2 **(b)**, but in such a case a force is generated parallel to the surface in addition to the normal vector. This force acting parallel to the surface may push and remove particle aggregates with low adhesion that have been already deposited as more particles fly out from the nozzle. The mechanisms caused by oblique incidence prevent films with low adhesion from being formed on the Ti plate. Thus, at incident angles of 40° and 60°, particle aggregates were removed by the oblique incidence effect and fine HA films with good adhesion were formed by the deposition of submicron-size particles. As the cross section shown in Fig. 3 (b) also suggests, fine HA film was found to be produced by the oblique incidence effect since particle shape was not observed for 60°.

The XRD patterns of the HA film formed at 40° and of the HA particles used in this study are shown in **Figs. 5 (a)** and **5 (b)**. The crystallinity of the HA is retained throughout the process. The XRD patterns for 0°, 20° and 60° also indicate that the crystallinity was retained.

4. Conclusion

We produced an HA film on the Ti plate by the ADM and investigated the effect of varying incident angle of the beam on the HA film formation. Although the HA film's thickness was decreased and the roughness of the surface was modified as the incident angle increased, adhesion strength between the HA film and the Ti plate was increased. In the images of the HA film's cross section, particle's shape was observed for normal incidence, but it was not observed for the incident angle of 60°. We have found that oblique incidence effect improved the adhesion strength and cohesive strength of the HA film. The crystallinity of HA film is retained over the process.

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