Formation of highly oriented hydroxyapatite in hydroxyapatite/titanium composite coating by radio-frequency thermal plasma spraying

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Highly oriented hydroxyapatite (HA) coatings with excellent adhesion were successfully obtained on titanium (Ti) and titanium alloy through a radio-frequency thermal plasma spraying method. The ratio of HA and Ti powders supplied into the plasma was precisely controlled by two microfeeders so as to change the composition from Ti-rich to HA-rich toward the upper layer of the formed coatings. The bond (tensile) strength of the HA/Ti composite coatings was ca. 40–50 MPa. XRD patterns showed that the topmost HA layer of the coatings had an apatite structure with (00*l*) preferred orientation. The degree of this orientation showed a tendency to increase with an increase in the substrate temperature during spraying.

1. Introduction

Plasma-sprayed hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ (abbreviated as HA) coated on titanium alloy substrates has been medically applied to promote the osteoconductivity of implanted materials [1, 2]. For practical medical application, there is a strong demand for HA coatings demonstrating both sufficient stability inside the human body and excellent adhesion to the substrate. In addition, it is particularly important for biomaterial applications that such HA coatings are not contaminated by toxic materials. Among the various coating methods, which include sputtering, chemical deposition, electrophoresis, slurry dipping and flame spraying, the thermal plasma spraying (TPS) method has been seen as advantageous in giving a relatively higher bond strength between the substrate and coating. Moreover, for medical application, the radio-frequency (RF)-TPS method has an advantage over the direct current (DC)-TPS method since contamination of the HA coating by toxic materials, such as copper and tungsten compounds from electrodes, can be avoided [3]. However, due to the large difference in thermal expansion coefficients between ceramic coatings and metal substrates, residual stress arises at their interface. In the case of HA coating on Ti 6Al–4V alloy, such residual stress is estimated to be in the range of ca. 20–40 MPa (tensile) [4]. Such residual stress may generate cracks in coatings and weaken their adhesion to the substrate. Therefore, conventional DC-TPS methods have been limited in achieving strong adhesion of HA coatings within the 50-μm in thickness to roughened metal substrates (e.g. grit blasted surface [5–7]). Recently, we have developed a new RF-TPS method that allows us to obtain strong adhesion between coatings and substrates without the above limitations [7, 8].

It has been reported that plasma-sprayed HA coatings have slowly dissolved *in vivo* [9]. In particular, during the initial 10 months of the implantation period, HA coatings have been seen to degrade logarithmically until a stable bone/coating interface forms [10]. For this reason, the solubility control of plasma-sprayed coatings is considered vital to promote early healing. It is well known that HA crystals both in long bones and in tooth enamel are highly oriented in the direction of their *c*-axis. This orientation has been thought to contribute to the chemical stability of HA crystals *in vivo* [11]. If HA crystals with such orientation could be produced in a HA/Ti composite by RF-TPS, these coatings might be highly reliable in medical applications. Here we briefly describe a method which promises to simultaneously satisfy both this demand for crystal orientation and for strong adhesion.

2. Experimental methods

Our technique for preparing the HA/Ti composite coatings was based on precise control of the starting composition by means of two microfeeders which made it possible to feed the HA and Ti powders at an accurate rate [7, 8]. The starting composition was regulated so as to change gradually from Ti-rich at the bottom layer to HA-rich at the top. In order to compare the adhesion of the HA/Ti coating layer to the substrate, we also prepared two other types of coatings, that is, HA coatings without Ti powder (direct HA coatings) and HA coatings on plasma-sprayed Ti substrate (HA/Ti bilayer coatings).

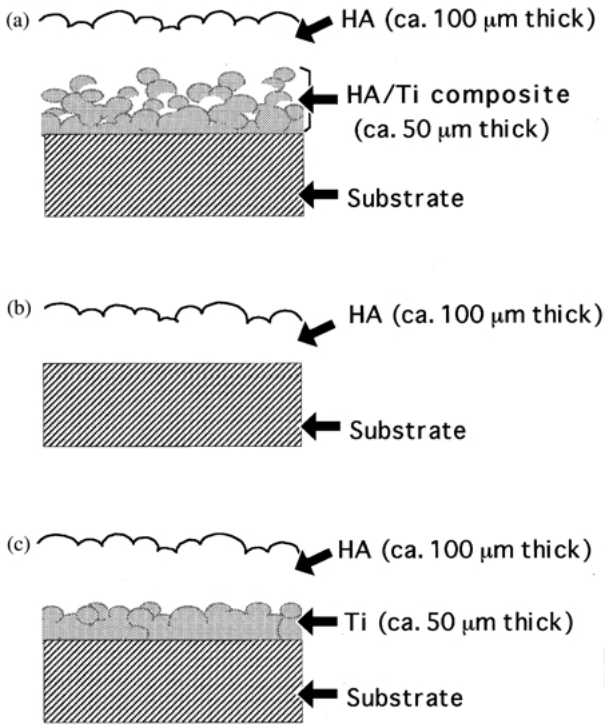

Figure 1 Schematic diagrams of the coatings prepared in this study. (a) HA/Ti composite coating, (b) direct HA coating, (c) HA/Ti bilayer coating.

TABLE I Experimental conditions

RF input (kW)	11–27
Frequency (MHz)	4
Plasma gas	argon
Plasma gas flow rate (l/min)	50
Pressure (Pa)	6.7×10^4
HA powder feed rate (g/min)	0–0.1
Ti powder feed rate (g/min)	0.15–0
Carrier gas	argon
Carrier gas flow rate (l/min)	7
Spray distance (cm)	28–35

Fig. 1 shows schematic diagrams of these three types of coatings. Hydroxyapatite powder (80 μm in diameter, Pentax) and titanium powder (< 325 mesh pass, 99.9%, Nilaco) were used as raw material. Commercial titanium plates (0.8-mm thick, ASTMB348-GR2) and commercial titanium alloy plates (0.8 mm thick, SP700, NKK) were polished with #400 SiC abrasive paper, washed ultrasonically in acetone and ethyl alcohol, and then dried in air before spraying. The composition of SP700 is 88.5% (mass) Ti, 4.5% Al, 3% V, 2% Fe and 2% Mo. An RF-TPS apparatus (Nihon Koshuha Co., Ltd, Japan) with a set of 4 MHz–35 kW power units (Nihon Koshuha Co., Ltd, Japan) was employed. The experimental conditions for the RF plasma spraying are summarized in Table I. A thermal plasma of Ar gas with the addition of O_2 gas was generated at 4 MHz frequency with input power of 11–27 kW. HA and Ti powders were fed axially into the plasma and deposited onto the substrates. In this study, the substrate temperature, measured by a Pt/Pt · 13Rh thermocouple, was proportional to both the RF input and the concentration of the added O_2 gas. Thus, the substrate temperature was controllable by both the composition of the plasma gas and by the RF input.

The topmost HA layer of the HA/Ti composite coatings was evaluated by X-ray diffraction (XRD) (MPX^3, MAC Science, Japan). Coating bond strength was measured by an autograph-testing machine (AG-500A, Shimazu, Japan). In this measurement, carbon steel rods (CS45, 8 mm in diameter) were bonded to both the coated and the uncoated sides of each sample with epoxy glue (SW 2214, 3 M). An alignment jig was used to achieve axial alignment of the two rods. After the epoxy glue was hardened at 130 °C for 8 h, a tensile stress was applied to the coating layer at a crosshead speed of 0.5 mm/min.

3. Results and discussion

HA/Ti composite coatings over 150 μm thick were successfully obtained using our present method. Fig. 2 shows the bond (tensile) strength of the HA/Ti composite coatings compared to that of the other two types of coatings prepared. The average bond strength for the HA/Ti composite coatings was over 40 MPa. After spraying at the RF input power of 17 kW, bond strength was 50.2 MPa with a standard deviation of 5.5.

With the direct HA coatings, the ca. 100-μm thick HA coatings which we obtained often peeled off after plasma spraying. As shown in Fig. 2, the average bond strength value for the direct HA coatings (100 μm thick) was under 5 MPa. The 100 μm thick HA coatings on the priorly deposited pure-titanium coatings had an average bond strength of 23 MPa. This improvement in adhesion for the bilayer type coatings may be attributable to mechanical interlocking at the rough HA/Ti interface. The adhesive strength of the HA/Ti composite coatings was over 10 MPa greater than that of either of the other coatings examined here. Since the texture of the HA/Ti composite coating is more intricate than that of the bilayer coating, the composite coating can be expected to generate stronger mechanical interlocking. Moreover, the HA/Ti composite interlayer may relax residual stress,

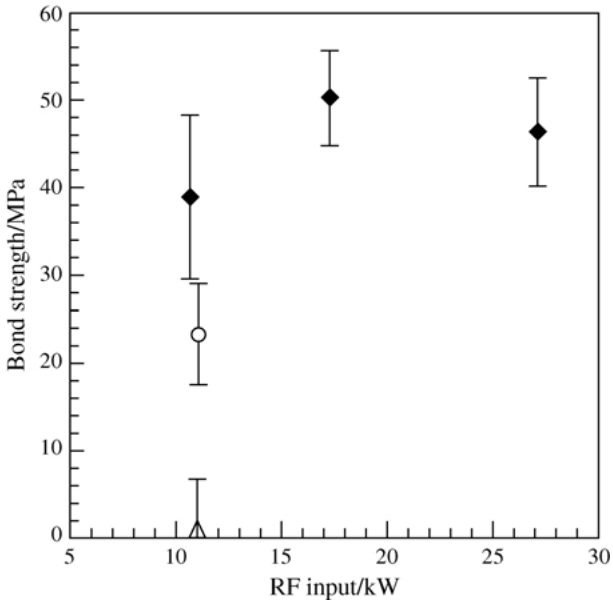

Figure 2 Plots of adhesive strength against RF input power during RF-TPS. ◆, HA/Ti composite coatings; ○, HA/Ti bilayer coatings; △, HA direct coatings.

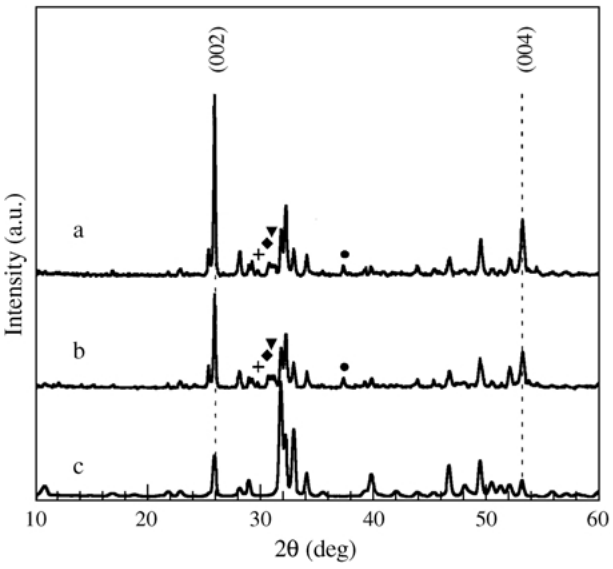

Figure 3 XRD patterns of the topmost HA layer of HA/Ti composite coatings plasma-sprayed with an rf input power of 17 kW at the substrate temperatures of 1000 °C (a) and 900 °C (b). An XRD pattern of the raw HA powder (c) is also shown for comparison. +, TeCP; ◆, α-TCP; ▼, β-TCP; ●, CaO.

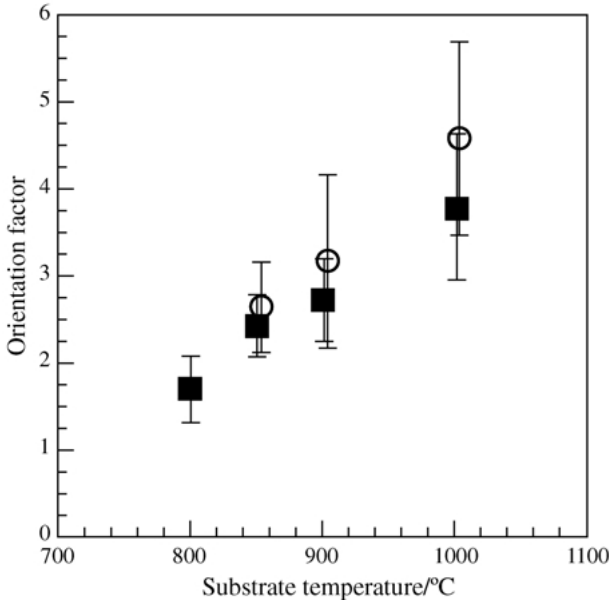

Figure 4 Orientation factors F_{ori} of the topmost HA layer versus the substrate temperature during RF-TPS. RF-TPS of the HA/Ti composite coatings was conducted at 17 kW (○) and 27 kW (■).

which often generates cracks in conventional coatings reducing the reliability of plasma-sprayed HA coatings on Ti or Ti alloy substrates. In our present experiment, bond strength was unaffected by differences between the Ti and Ti alloy substrates.

The XRD patterns of the surface HA layer of the HA/Ti composites shown in Fig. 3 indicate that the apatite structures have $(00l)$-preferred orientations parallel to the substrate. An XRD pattern of raw HA powder is also shown in Fig. 3 for comparison. Some minute X-ray peaks ascribable to tetracalcium phosphate (TeCP), α-tricalcium phosphate (α-TCP), β-tricalcium phosphate (β-TCP), and calcium oxide (CaO) can also be observed. In this study, we calculated the orientation factor F_{ori} by the equation proposed by Kameyama *et al*. [12], which is expressed as:

$$F_{ori} = \left\{ \sum I_C(00l) \Big/ \sum I_C \right\} \Big/ \left\{ \sum I_R(00l) \Big/ \sum I_R \right\} \quad (1)$$

where $I(00l)$ is the peak intensity of the $(00l)$ planes in the HA and I is the intensity of the HA diffraction peak. The subscripts C and R denote the diffraction of the HA coating and the reference HA powder, respectively. HA XRD peaks located in the 2θ range of 20–60 ° were chosen to calculate F_{ori}.

Fig. 4 plots the calculated F_{ori} versus the substrate temperature. As clearly shown, F_{ori} increases with an increase in the substrate temperature. On the other hand, these values show close agreement regardless of the RF input power during spraying. This implies that the crystal orientation was significantly influenced by the substrate temperature, which may affect the solidification of the quasi-molten HA particles after deposition. Kameyama *et al*. have reported $(00l)$-preferred orientations of HA coatings sprayed on partially stabilized zirconia. They also proposed that such c-axis orientation in a plasma-sprayed HA coating is due to a unidirectional crystallization process occurring under a high-temperature gradient [12, 13]. During such unidirectional crystallization, substrate temperature is likely to play a major factor in the nucleation and growth of the HA crystals.

4. Conclusions

We have successfully formed highly oriented HA coatings on titanium and titanium alloy substrates. Our results presented here indicate that the HA/Ti composite coatings demonstrated significantly improved adhesion over plasma-sprayed HA coatings. HA/Ti composite coatings obtained at RF input power of 11 kW gave an average bond (tensile) strength of ca. 40 MPa. HA composite coatings sprayed at 17 kW exhibited bond strength of 50.2 MPa. The HA crystals in these HA/Ti composite coatings were oriented in the direction of their c-axis. Their degree of c-axis orientation showed a tendency to increase with the substrate temperature during RF-TPS.

The solubility of such coatings is influenced not only by their crystal orientation, but also by other coating characteristics, such as crystallinity and composition [14]. Since these characteristics are influenced by RF-TPS processing parameters [15], they can be controled to a certain extent by simply varying these parameters. Moreover, coating crystallinity and composition can also be controled by post-treatment, such as by heat [16, 17]. These techniques could be combined together with our HA/Ti composite coating method employed here to fabricate strongly adhesive, biocompatible coatings on titanium or titanium alloy for artificial joint replacement prostheses and other medical applications.

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