



## Production of “Tricalcium Phosphate/Titanium Dioxide” Coating Surface on Titanium Substrates

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A new method for the production of the coating surface consisting of tricalcium phosphate (TCP) and titanium dioxide (TiO<sub>2</sub>) on titanium (Ti) substrates by using electrophoretic deposition (EPD) method has been developed. Crack occurrence on coating surface and hydroxyapatite (HA) decomposition into TCP, which are commonly encountered in EPD method, were used as an advantage in this study. HA nano-powders synthesized by acid-base method were used as the coating material. They were deposited on Ti substrates with different voltages and durations. Cracks on the deposited surface were observed by scanning electron microscopy (SEM). Samples were sintered in air atmosphere to allow TiO<sub>2</sub> growth from the Ti substrate to fill the cracks. SEM observation and X-ray diffraction (XRD) analysis proved the occurrence of complete decomposition of HA into TCP, TiO<sub>2</sub> growth between cracks, and coalescence of TCP/TiO<sub>2</sub> on coating surface. This type of coating surface is expected to increase the coating strength because of TiO<sub>2</sub> growth in the cracks and its coalescence with TCP.

**KEY WORDS:** Electrophoretic deposition; Hydroxyapatite; Bioceramics; Microstructure

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### 1. Introduction

Calcium phosphate (Ca-P) based ceramics have been proven to be attractive materials for biological applications. Among these bioceramics, particular attention has been given to hydroxyapatite (HA), Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>, and tricalcium phosphate (TCP), Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, due to their outstanding biological responses to physiological environments. Because of its close similarity in chemical composition and high biocompatibility with natural bone, synthetic HA exhibits strong affinity to host hard tissues<sup>[1,2]</sup>. On the other hand, TCP has been proven to be resorbable *in vivo* with new bone growth replacing the implanted TCP<sup>[3,4]</sup>.

Application of Ca-P based ceramics in the human body has been limited due to their poor mechanical properties<sup>[5]</sup>. Unlike Ca-P based ceramics, tita-

nium (Ti) and Ti-alloys are proven to be potentially very suitable materials for load bearing bioimplant applications<sup>[6]</sup>. The concept of coating metal implant surfaces with Ca-P based ceramics combines the mechanical benefits of metal alloys with the biocompatibility and biointegration of Ca-P based ceramics. Coating biologically inert metallic implants with biologically active materials is an attempt to accelerate bone formation at initial stages of osseointegration, thus improving implant fixation<sup>[6,7]</sup>.

Many coating techniques have been employed for the preparation of HA coatings, such as plasma spraying, dip coating, chemical solution deposition, sputter coating, biomimetic coating, sol-gel and electrophoretic deposition<sup>[8-12]</sup>. The electrophoretic process exhibits some advantages over other alternative processes, such as simplicity of setup preparation, low equipment cost and the capability to form complex shapes and patterns homogeneously<sup>[6,13]</sup>. A high degree of control of coating deposit morphology can be obtained by adjusting deposition conditions and

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powder size and shape of the ceramic<sup>[14,15]</sup>. However, the bonding strength between coating and metal substrate is weak, which necessitates post-sintering. Although the sintering process improves coating adhesion onto the substrate, it can promote crack occurrence on coating surfaces and HA decomposition<sup>[14,16]</sup>. When HA coatings obtained by electrophoretic deposition (EPD) are sintered at temperatures above 900°C, partial transformation of HA into other Ca-P phases, especially to TCP can be observed<sup>[14,17,18]</sup>. Compared with HA, TCP has a lower calcium/phosphorous ratio, which increases the degradation rate when the ceramic is placed in a biological environment<sup>[19]</sup>. Implanted ceramics degrade allowing bone in-growth and eventual replacement of the artificial material with natural tissue<sup>[20]</sup>.

Crack occurrence on coating surface is detrimental for the achievement of the implantation since it decreases the coating strength. For practical medical applications, Ca-P coatings with adequate strength have been strongly demanded to provide long-time fixation<sup>[8]</sup>.

In the current study, a new method is developed to create TCP/TiO<sub>2</sub> coating surface on titanium substrates, where the TCP matrix is expected to be responsible for the adsorption of organic substances, and where the TiO<sub>2</sub> is responsible for strengthening the coating layer. HA nano-powders were produced and used in the EPD as the coating material. Different applied voltages (50 and 100 V) and deposition durations (30 and 60 s) were used in the deposition process. Deposited samples were sintered in air atmosphere in order to obtain TiO<sub>2</sub> growth (from Ti substrates) between cracks.

## 2. Experimental

### 2.1 Production of HA powders

In order to synthesize HA powders chemically, acid-base method was preferred due to its advantages over other methods: the reaction involves no foreign element and the only by-product is water. The procedure described by Wei *et al.*<sup>[21,22]</sup> was as follows. 5.0 g of Ca(OH)<sub>2</sub> (~99%, Merck, Germany) was dissolved in 200 ml of deionized water by using a magnetic stirrer. 4.669 g of liquid H<sub>3</sub>PO<sub>4</sub> (85%, Merck, Germany) was added slowly (to maintain pH>9.5–10) to the Ca(OH)<sub>2</sub> solution while the solution was continuously stirred by the magnetic stirrer. The pH value of the solution was continuously monitored by using a pH meter (Orion 4 star model, Thermo, USA). Stirring was continued at 30°C for 24 h after H<sub>3</sub>PO<sub>4</sub> addition. Then centrifugation, supernatant decantation and resuspension in deionized water were applied 5 times. The obtained precipitates were oven-dried at 80°C for 24 h followed by light grinding by hand with an agate mortar and pestle.

### 2.2 Electrophoretic deposition

The obtained HA powders were used as coating material. 0.5 g of powder was added into 80 ml ethanol (96%, Merck, Germany). After magnetically stirring for 15 min, suspensions were dispersed ultrasonically at 40 kHz for 30 min in an ultrasonic bath (Everest Elektromekanik, Turkey), and then suspensions were left to rest for 30 min to eliminate the bigger or agglomerated particles by sedimentation. Finally suspensions were ultrasonically dispersed again for 30 min to ensure a good dispersion of the particles<sup>[11]</sup>.

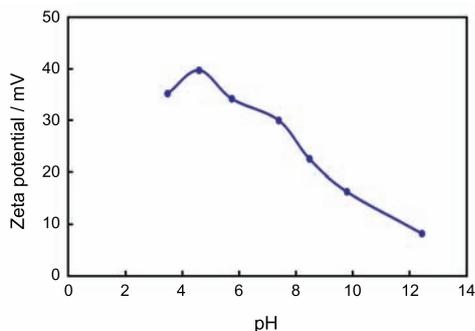
Titanium (grade 4, pure titanium) substrates of 15 mm×25 mm×2 mm in dimension were polished from 240 to 1000 grid SiC papers followed by the use of 1 μm diamond paste to get a mirror finish. Before deposition, substrates were thoroughly washed with detergent in ultrasonic bath for 30 min, followed by washing in acetone (extra pure, Merck, Germany) for another 20 min, and then passivated in 25 vol. pct nitric acid (65%, Merck, Germany) overnight, and then washed in distilled water<sup>[11,14]</sup>.

The pH values of the suspensions were adjusted to approximately 4 according to their zeta potential analysis results. At this stage, HA particles acquired positive charge and their deposition occurred at the cathode. The titanium electrodes were placed parallel to each other in the suspension, with a distance of 10 mm approximately, and connected to a DC power supply (Model AE-8150, Atto, Japan). The EPD process was performed under constant voltages of 100 V for 60 s, 50 V for 60 s, and 50 V for 30 s, respectively. After deposition, the green form coatings were dried at room temperature, and then sintered in a tube furnace at 1000°C for 2 h in air atmosphere at a heating rate of 100°C/h and cooling rate of 50°C/h.

Sintering temperature should be selected as low as possible in order to minimize the deleterious effects on titanium. Titanium is reactive at high temperatures and oxidizes easily. Since oxygen diffuses easily in titanium and the dissolved oxygen embrittles the metal, high sintering temperatures led to the embrittlement of the metal substrates and resulted in reduced mechanical properties<sup>[22]</sup>. However, at low sintering temperatures, required densification and sufficient coating strength could not be obtained. Therefore sintering temperature should be selected as high as possible in order to obtain denser microstructure and to improve adhesion strength. Based on the previous experience of the current authors<sup>[11,23]</sup> and the literature [13,24] on the microstructure and densification of the coating layer, 1000°C was determined and used as the sintering temperature.

### 2.3 Characterization

The phase purity and constitution of the synthesized powder and obtained coating layer were inves-



**Fig. 1** Zeta potential as a function of pH for HA/ethanol suspension

tigated by X-ray diffraction (XRD) (Model D/Max-Ultima + PC, Rigaku, Japan). The XRD data were collected at room temperature over the  $2\theta$  range of 10–70 deg. at a step size of 0.02 deg. and a count time of 0.6 s.

Zeta potential analysis (Model Nano-ZS, Malvern, England) was performed in the pH range of 3–12 to determine the proper pH value used in the electrophoretic deposition. NaOH and HCl were used for pH adjustment; and ethanol was used as dispersant.

The morphology of the coating layers were observed by scanning electron microscopy (SEM, Model Supra 35VP, Leo, Germany) at an accelerating voltage of 2 kV. Prior to SEM examination, all the samples were dried at 80°C overnight, and sputter coated by carbon to minimize any possible surface charging effects. The images were obtained for the coating layers before and after the sintering stage.

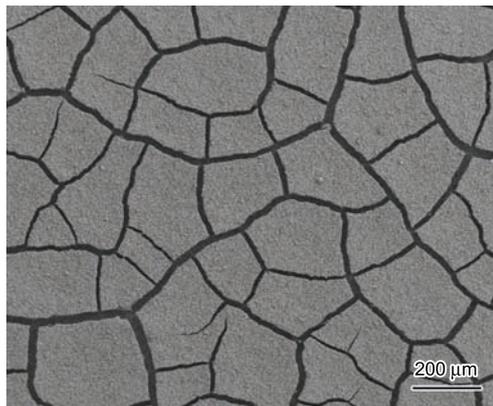
Scanning electron microscopy-energy dispersive X-ray (SEM-EDX) analyses and energy dispersive X-ray spectrometer (EDX) mapping were performed to visualize the elements Ca, P, Ti and O across the coating surface.

### 3. Results and Discussion

The method mentioned in the section 2.1 was used in a previous study of the current authors<sup>[25]</sup>, and HA nanoparticles (~120 nm by ~40 nm) of needle-like shapes (ICDD PDF No: 84-1998; no other phases than HA) were produced by using this procedure.

The HA powders were used to prepare coating suspension for EPD. To determine the proper pH value for EPD, zeta potential analyses were performed, and zeta potentials as a function of pH for HA/ethanol suspension were obtained. Zeta potential values were over 30 mV for the pH range of 3–5 as shown in Fig. 1. Since high absolute zeta potential value indicates the presence of a well-dispersed suspension<sup>[26]</sup>, pH values of suspensions were adjusted to approximately 4.

The prepared suspensions were used in coating stage and HA particles were electrophoretically deposited on Ti substrates using 100 V for 60 s, 50 V for 60 s and 50 V for 30 s, respectively. For all of the samples, cracks were observed on

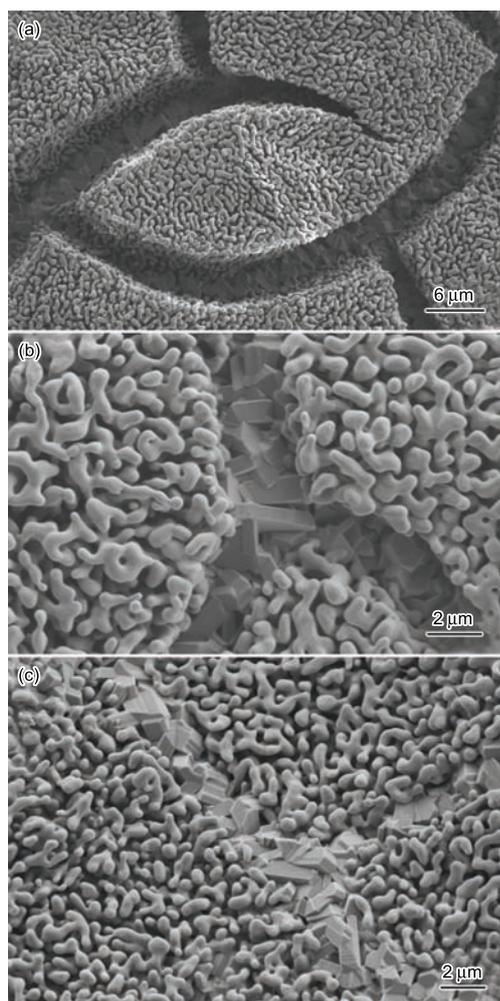


**Fig. 2** SEM image of coating surface (50 V for 60 s) before sintering stage

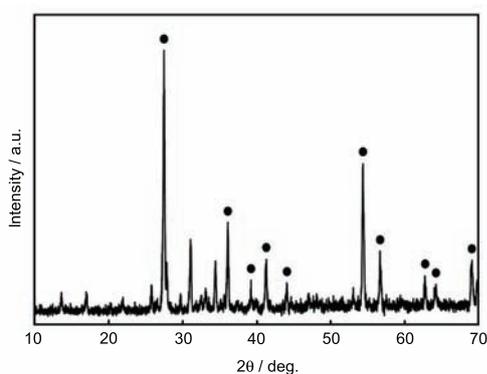
coating surfaces (Fig. 2). Literature [14, 21] states that use of HA particles synthesized by acid-base method in EPD process results in crack occurrence in coating layer. These types of cracks arise as a result of shrinkage during drying<sup>[25]</sup>. Crack occurrence tendency increases in sintering stage. Because of densification during sintering, shrinkage and cracking of the coatings may occur. Also thermal stress induced by differences in thermal expansion coefficients between metal and the ceramic film during sintering and cooling leads to cracking<sup>[14,22]</sup>. In order to cover the cracks on coating surface, dual coating was studied by Wei *et al.*<sup>[14]</sup>. In the study of literature [14], a cycle consisting of consecutive coating and sintering steps were applied twice, and it was observed that surface cracks, which occur in the first coating layer were covered by the second coating layer. Although obtaining a crack-free coating surface using dual coating is possible, another sintering stage must follow the second coating step, which doubles the processing time. In the current study, it is aimed that cracks were covered by the TiO<sub>2</sub> growth from Ti substrate. In order to obtain TiO<sub>2</sub> formation on Ti substrates in the cracks, deposited samples were sintered in air atmosphere. As predicted, TiO<sub>2</sub> growth was observed inside the cracks (Fig. 3) all over the surface.

Different applied voltages and deposition durations were studied in order to allow TiO<sub>2</sub> growth in cracks up to coating surface. It was determined that 100 V for 60 s (Fig. 3(a)) is not suitable for the TiO<sub>2</sub> growth up to coating surface because of the resulting thick coating layer. Therefore, smaller voltages and shorter durations were applied since coating thickness decreases with the applied voltage and deposition time. Although more satisfactory results are obtained by using 50 V for 60 s (Fig. 3(b)), 50 V for 30 s (Fig. 3(c)) was found to be sufficient for TiO<sub>2</sub> growth up to coating surface.

XRD spectra and results of phase identification for the coating surface (deposition parameters: 50 V for 30 s) after sintering stage are presented in Fig. 4. It revealed that the sintered coating was composed

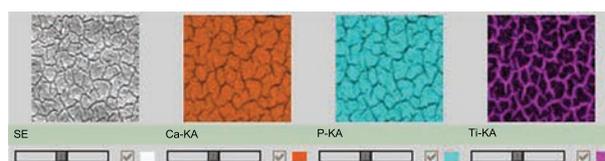


**Fig. 3** SEM images of coating surfaces after sintering stage in air atmosphere ( $\text{TiO}_2$  growth in the cracks): (a) 100 V for 60 s, (b) 50 V for 60 s, (c) 50 V for 30 s

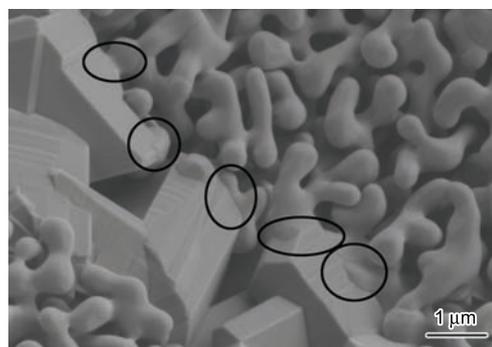


**Fig. 4** XRD spectra of coating surface for 50 V 30 s (● are used for  $\text{TiO}_2$ ; all other unsigned peaks are TCP)

of rutile  $\text{TiO}_2$  (ICDD PDF No: 77-441) and  $\beta$ -TCP phases (ICDD PDF No: 9-169). Sintering of the HA coated Ti substrates at  $1000^\circ\text{C}$  for 2 h induced complete decomposition of HA into TCP for the samples



**Fig. 5** EDX mapping of coating surface for 50 V 30 s



**Fig. 6** Coalescence of TCP/ $\text{TiO}_2$  on coating surface

obtained by using 50 V for 30 s as deposition parameters. Atomic percents of Ca and P were determined as 60 and 40, respectively ( $\text{Ca}/\text{P}=1.5$ ) by quantitative EDX analysis showing the presence of TCP phase in support of the XRD data. Since TCP has a higher degradation rate than HA<sup>[20,27,28]</sup> and since degradation of implanted ceramics allows bone in-growth and eventual replacement of the artificial material with natural tissue<sup>[20]</sup>, decomposition of HA into TCP is thought to be advantageous.

EDX mapping (Fig. 5) of these sintered samples were used to show the presence of Ca, P and Ti on the coating surface. These elemental scans revealed that Ca and P were determined at the surface except the cracks, where Ti was visualized.

SEM micrograph (Fig. 6) revealed that coalescence between TCP and  $\text{TiO}_2$  was obtained. This type of coating surface is expected to increase the coating strength due to  $\text{TiO}_2$  growth and its coalescence with TCP can hinder the shear.

Overall coating strength can be discussed when Figs. 2, 3(c), 5 and 6 are taken into account. Considering the area on which the forces are applied in the shear strength (ASTM F 1044-05: standard test method for shear testing of calcium phosphate coatings and metallic coatings) and tensile strength (ASTM F 1147-05: standard test method for tension testing of calcium phosphate and metallic coatings) tests, the cracks in the coating surface (as presented in Fig. 2) would result in a decrease in strength since they introduce a discontinuity on the coating surface and decrease the overall surface area of the coating. On the other hand, when the cracks are filled with  $\text{TiO}_2$  (as presented in Figs. 3(c) and 5), the overall surface area of the coating increases; thus an increase in the strength value is expected. Moreover, coalescence between coating and the crack-filling material

as presented in Fig. 6 is expected to cause further increase of both the shear and the tensile strength values.

#### 4. Conclusions

The newly developed simple and inexpensive process allows forming coating surfaces consisting of TCP and TiO<sub>2</sub> on Ti substrates by a single step. In the present study, HA powders produced by acid-base method were coated on titanium substrates by EPD method. Besides the advantages of the precipitation method, cracks on coating surfaces were obtained as mentioned in literature. After sintering at 1000°C for 2 h, TiO<sub>2</sub> growth from Ti substrates in cracks were observed. It is determined that using 50 V for 30 s as deposition parameters is suitable for TiO<sub>2</sub> growth up to the coating surface in order to fill in the cracks.

XRD spectra and results of phase identification showed that peaks of the formation between cracks were completely matched with the rutile-TiO<sub>2</sub>. EDX mapping analysis of sintered samples visualized the presence of Ca and P at the surface except cracks, where Ti was determined.

XRD analysis of sintered coating revealed that HA completely decomposed into TCP, which is expected to be progressively digested by surrounding tissue. The progressive digestion of the TCP by living tissue will potentially promote the tissue in-growth and allow implant-tissue integration by biological fixation.

SEM micrographs illustrated that coalescence between TCP and TiO<sub>2</sub> was obtained at coating surface. This is expected to increase the adhesion strength of coating compared to a coating with surfaces cracks.

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