Effects of TiO_2 Contents on HA/TiO_2 Composite Coating by Electrophoretic Deposition

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Abstract. The HA composite coating with different TiO_2 contents was prepared by electrophoretic deposition in this study. The composite coatings were characterized by scanning electron microscopy (SEM), Ca/P atomic ratio in composite coatings was analyzed by Energy Dispersive Spectrometer (EDS), and the adhesion strength was analyzed by Universal Material Testing Machine. The results show that the density of HA-TiO_2 composite coatings was elevated with increasing TiO_2 contents after sintering at 850˚C. The atomic ratio of Ca/P (calcium and phosphorus) of the HA/TiO_2 composite coatings showed a rising trend with the increasing contents of TiO_2 in suspensions. The atomic ratio of Ca/P was 1.69 and 1.75 which was close to the human bone (1.67), when the TiO_2 content was 10g/L and 15g/L in the suspension, respectively. The thickness of the coatings increased with the TiO_2 contents increasing, which was 30μm that deposited in the suspension content with 10g/L TiO_2, and great combination was shown with the good uniformity of the coating. The adhesion strength was 9.10MPa as the TiO_2 content was 10g/L.

Introduction

The hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HA), is an inorganic constituent of the human bones, which can induce the growth of new bone[1-2]. It is a biomedical ceramic material that was widely used in material substitute to human hard tissues to improve the cell responses and osteo-conductivity, which can easily form a bond with the neighboring bone after planted in the human body; meanwhile, it is non-toxic, high bioactivity and high biocompatibility [3-4].

Electrophoretic deposition (EPD) is an economical technique for the preparation of uniform HA coatings on titanium alloy substrate. The EPD technique has several advantages compared to other common methods of surface coating, including short formation time, simple apparatus and the shape of substrate is unconstrained etc.[5]. However, some shortage of the EPD method limited its application, such as the HA coatings is easy to thermal decompose into tricalcium and tetracalcium phosphates when the sintering after deposition at a high temperature, the sintering temperature should be set below 1000°C to retard the decomposition of HA coating[6]. What's more, the adhesion strength between HA and substrate is not high enough because of the mismatch of thermal expansion coefficient (CPE) between titanium ($\alpha_{Ti}=8.7\times10^{-6}K^{-1}$) substrate and HA coatings ($\alpha_{HA}=(14\sim16)\times10^{-6}K^{-1}$) [7]. The results showed that the transition of the HA coating that prepared between the substrate and the HA coating was with a proper thermal coefficient of expansion and can significantly improve the adhesion strength [8].

In this paper, the TiO_2 was selected as transition layer because of the thermal expansion coefficient of TiO_2 ($9.0\times l0^{-6}K^{-1}$) between titanium alloy and HA, and it can ease the residual stress. It will improve the performance of the combination between coating and the base. The functional HA-TiO_2 composite coating was fabricated by electrophoretic deposition and heat-treatment in the titanium substrate surface in order to study the effects of TiO_2 content on HA-TiO_2 composite coating performance.

Experiment

Experimental materials

Hydroxyapatite powder (30nm, Sinopharm Chemical Reagent, China) and TiO_2 powder (30nm, Sinopharm Chemical Reagent, China) were used as the raw materials. Ti-7.5Mo alloys (φ10×15mm) that prepared by gel-casting were used as metallic substrates in this study.

Preparation of the Suspension and Deposition

N-butyl alcohol (Sinopharm Chemical Reagent, China) was used as a solvent and the pH of the suspension was adjusted to 5.5~6.5 by adding triethanolamine. In this study, four suspensions were prepared with different TiO_2 contents, shown as Table1. The content of HA was kept at 10g/L (1g HA was added in 100ml N-butyl alcohol) in each suspension.

Table1. Preparation of the suspension for HA-TiO_2 graded composite coatings

Contents of TiO_2[g/L]	The amount of TiO_2 in the suspensions[g] (added in 100ml N-butyl alcohol)			
	Suspension a	Suspension b	Suspension c	Suspension d
5	0.5	0.3	0.1	0
10	1	0.6	0.2	0
15	1.5	0.9	0.3	0
20	2	1.2	0.4	0

Characterization Testing

The microstructure of the coating was characterized by SEM, and the thickness of the coating was measured by observing the cross section morphology of coating. Elemental analysis of coating was evaluated by EDS, and the coating's atomic ratio of Ca and P can also be calculated.

Schematics of adhesion strength of the coating were showed as Fig. 1. The coating and the titanium substrate was bonded with the stainless steels respectively. Tension was applied on stainless steels till the coating was peeled from the substrate. The adhesion strength was figured by the following formula.

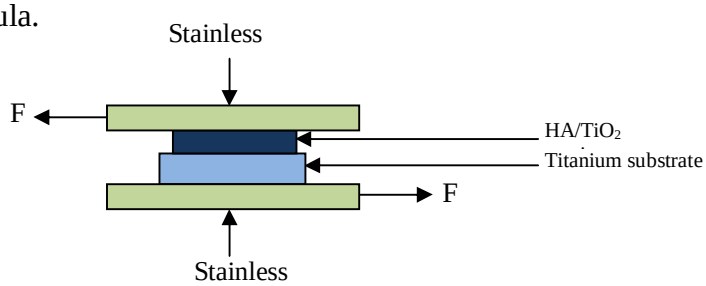

Fig.1. Schematic diagram of the adhesion strength test for the coating

$$\sigma = F/A \quad (1)$$

F- Maximum tension while coating peeled
A- Contact area of the stainless steel with the coating

Results and Discussion

Surface morphology and the Ca/P ratio of the HA/TiO_2 composite coatings

Fig.2 showed the surface morphology of the composite HA/TiO_2 coatings with different TiO_2 contents after sintering at 850˚C. As can be seen, the coatings became non-uniform when the TiO_2 content increased to 15g/L and 20g/L. In fact, with increasing of the TiO_2 contents, the pore size and the number of the pore on the coatings reduced, the coatings became more compact, because a closely packed accumulation of HA and TiO_2 particles could be formed during a short time and the bonding between the HA and TiO_2 particles were strengthen by increasing the TiO_2 contents. The coatings could be porous and loose when the TiO_2 content was kept at a low level. However, the coating surface became non-uniform, which may be caused by the high potential of TiO_2, the TiO_2 particles could be deposited more easy than the HA particles.

As can be seen in Fig. 3, there were little impurity elements on the surfaces of coatings. The atomic rate of calcium and phosphorus was 1.46 when the TiO_2 content was 5g/L in the suspension, which was less than the human bone (~1.67)[9] and illustrated that the crystalline of HA was not enough. When the TiO_2 content was 10g/L and 15g/L, the Ca/P atomic rate was 1.69 and 1.75 respectively, which was close to the human bone and what can be seen that the appropriate TiO_2 content in the suspension could promote the ossification of HA. However, when the TiO_2 content was 20g/L, the Ca/P atomic rate was up to 1.92.

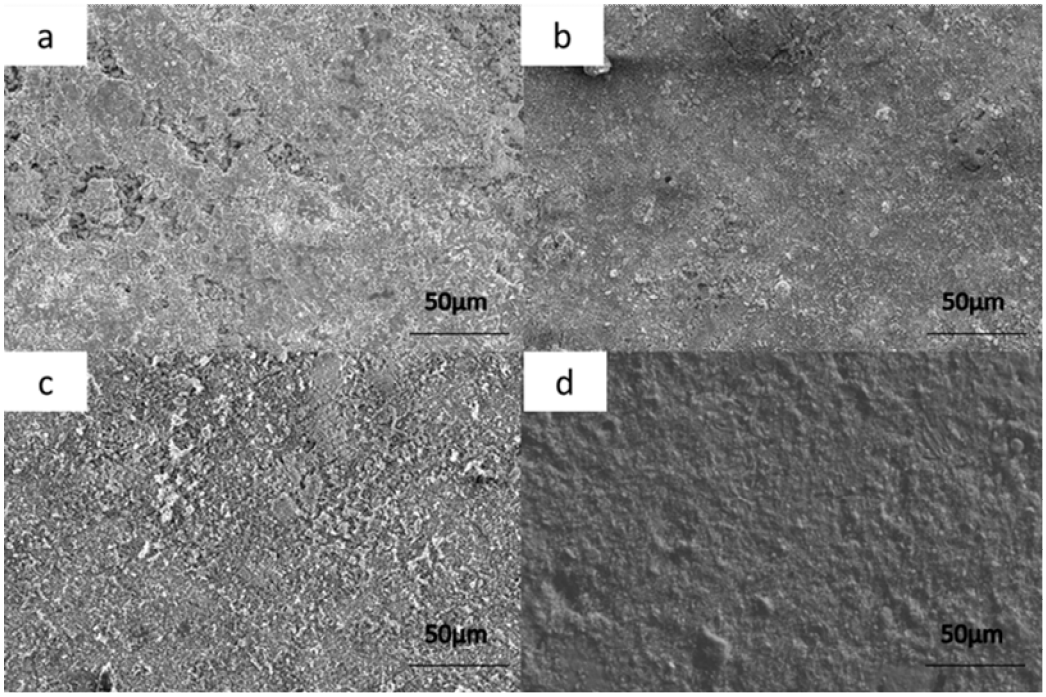

Fig.2. SEM images of the coatings deposited from the suspensions with 10 g/L HA and different TiO_2 content (500×): (a 5g/L, b10g/L, c 15g/L, d 20g/L) after sintering at 850˚C, respectively

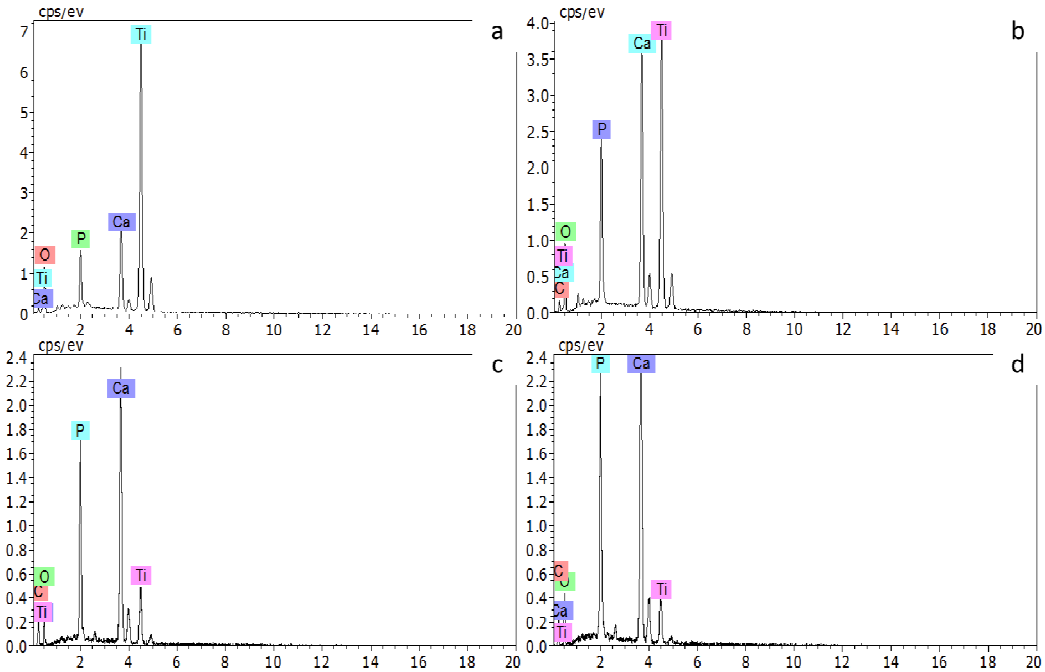

Fig.3. EDS of HA/TiO_2 coatings with different TiO_2 contents (a 5g/L, b10g/L, c 15g/L, d 20g/L) after sintering at 850˚C

Cross Section SEM micrograph of HA/TiO_2 coating

Fig. 4 was the cross section SEM micrograph of HA/TiO_2 coatings. It can be seen that the thickness of in the coatings increased as the TiO_2 contents increased. What can be known that the coatings were very uneven when the TiO_2 contents were 15g/L and 20g/L. What's more, the cracks were obvious, which could cause reducing adhesion strength greatly (Fig.4c and d). However, as can be seen thickness of coating was 25μm that deposited in the suspension content with 10g/L TiO_2, and great combination was shown with the good uniformity of the coating.(Fig.4b).

The adhesion strength of the coatings with different TiO_2 contents sintering at 850˚C were shown in Fig. 5. The adhesion strength of coating was merely 4.34MPa without any TiO_2, and the adhesion strength was increased from 6.85MPa to 9.10MPa while the TiO_2 content was increased from 5g/L to 10g/L. However, the adhesion strength was decreased when the TiO_2 content was 15g/L and 20g/L, which was 6.18MPa and 4.08MPa respectively, which may be caused by the obvious cracks on the coatings.

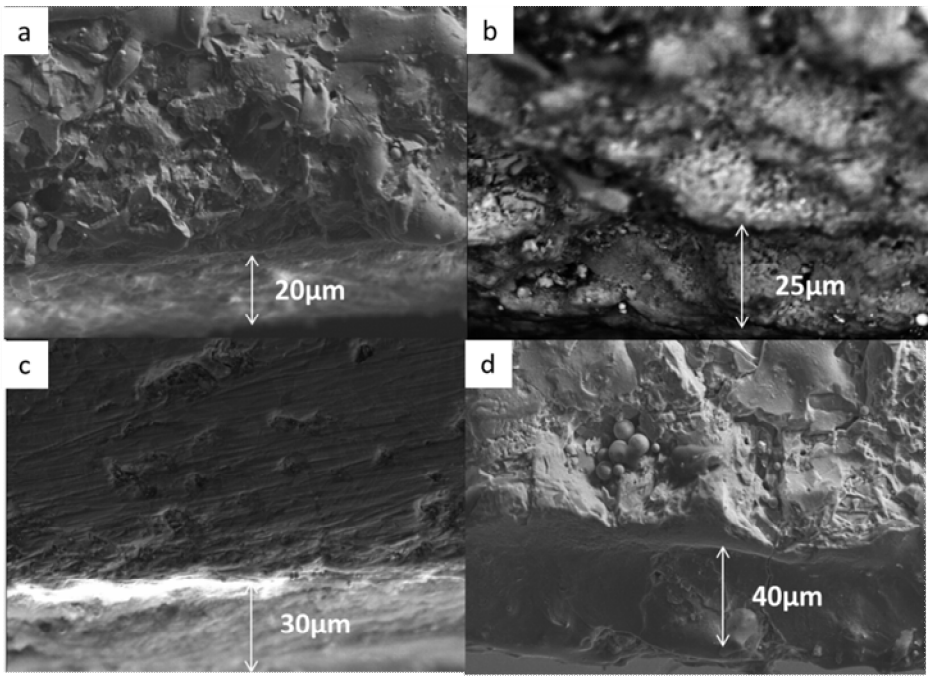

Fig.4. Cross section SEM micrograph of HA/TiO_2 coatings with different TiO_2 contents (a 5g/L, b 10g/L, c 15g/L, d 20g/L) after sintering at 850˚C

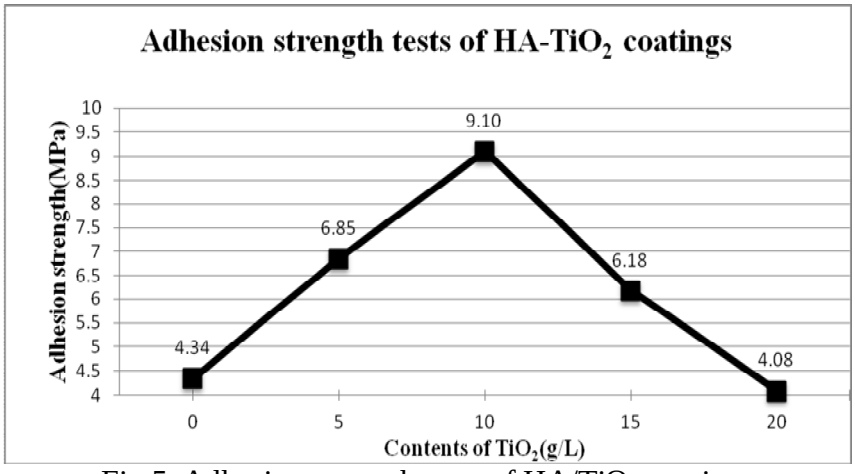

Fig.5. Adhesion strength tests of HA/TiO_2 coatings

Conclusion

The different TiO_2 contents composite coating was successfully prepared by electrophoretic deposition in this paper. The Ca/P atomic ratio of the HA/TiO_2 composite coatings showed a rising trend with the TiO_2 contents in suspensions increased. When the TiO_2 content in the suspension was 10g/L and 15g/L, the Ca/P atomic rate was 1.69 and 1.75 respectively, which was close to the human bone. The thickness of the coatings increased as the TiO_2 contents increasing. The thickness of coating was about 20μm that deposited in the suspension with the TiO_2 content of 10g/L, and great combination was shown with the good uniformity of the coating. The adhesion strength was 9.10MPa while the TiO_2 content was 10g/L.

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