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Preparation of a Hydroxyapatite/ β calcium phosphate coating with high bonding strength on a titanium substrate

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Hydroxyapatite/ β -calcium phosphate coatings with a high bonding strength on titanium substrates were prepared by electrodeposited-hydrothermal synthesis and calcination. The phase composition, microstructure and bonding strength of the coatings were studied by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and mechanical testing. It showed that electro-deposition coating phase mainly consisted of dicalcium phosphate dehydrate and hydroxyapatite. A single hydroxyapatite phase coating was obtained after a hydrothermal treatment for four hours in a solution of ammonia with a pH value above 12. After calcination below 700 °C, the phase composition of the coating remained the single hydroxyapatite phase. Then the β calcium phosphate phase appeared when the calcination temperature was above 800 °C. The quantity of β calcium phosphate could be controlled by adjusting the calcination parameters. For the specimens not pre-treated, calcination in air was beneficial to improve the bonding strength below 700 °C. Above 800 °C, the bonding strength decreased obviously because of the appearance of a loose and thick titanium nitride and titanium dioxide transition layer. The highest bonding strength in this study was obtained on the specimens pre-treated in a sodium hydroxide solution and calcined in an argon atmosphere at 900 °C.

Key word: Calcium phosphate, Hydroxyapatite, Coating, Hydrothermal treatment, Calcination, Bonding strength.

Introduction

Calcium phosphates [1] are widely used as biomedical materials, especially for osteological implantation, due to their identified biocompatibility. However their mechanical properties of brittleness, low tensile strength and fracture toughness restrict their application to non-load bearing areas of human bodies [2]. By contrast, titanium and titanium alloys [3] have a high strength, stiffness and impact resistance, and can be used for load bearing applications. However, titanium and titanium alloys have low bioactivity and a long time is needed to achieve an inter-gradation between implant and bone tissue [4].

For these reasons, calcium phosphate coatings on titanium substrates have been found wider applications [5, 6]. These composite materials combine the mechanical properties advantages of metal substrates with their bioactivity and biocompatibility of calcium phosphates. These materials prepared by a plasma spraying technique [7, 8] have a high bonding strength between the coating and the substrate. However, the plasma spraying technique is a line-of-sight process and involves a very high temperature, leading to a non-uniform coating and degradation of hydroxyapatite bioactive properties [9, 10]. Also, thermal stresses will be generated in the subsequent cooling process, which was initiate cracks in and peeling of the coating [11]. Electrodeposition [12, 13] is a method that can prepare calcium phosphates coating at low temperature, and the phase composition can be controlled by a hydrothermal treatment and calcination. This material has recently attracted considerable attention. But some studies report that the bonding strength between the coating and substrate is very low, and the long-term stability of this material is still questionable [14, 15]. This major shortcoming limits the application potential of the electro-deposition method. To overcome this problem, several attempts have been made. A dense and uniform fluoridated hydroxyapatite coating has been obtained to improve the bonding strength [16]. The increase in adhesion and the relief of thermal mismatch come from the formation of chemical bonding at the interface. Adding the titanium dioxide particles to a hydroxyapatite coating is another attractive method. The addition of the titanium dioxide particles can enhance osteoblast adhesion and induce cell growth [17]. Some previous studies show that a hydroxyapatite/titanium dioxide coating prepared through a hydrothermal-electrochemical method has a high bonding strength, because of a synergistic effect of co-deposition of hydroxyapatite and titanium dioxide [18, 19].

In this study, a titanium dioxide transition layer was prepared by pre-treating specimens and calcination in an argon atmosphere at 900 °C. The existence of a crack-free, homogeneous dense and constant pure titanium dioxide

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transitional layer could decrease the thermal stress in the preparation process, reinforced the metallurgical combination and increased the bonding strength obviously. The microstructure, phase composition of coatings and the transition layers were investigated. The bonding strengths between the coatings and the titanium substrates were evaluated.

Experimental

Pure titanium substrates, with dimensions of $\Phi 20 \text{ mm} \times 2 \text{ mm}$, were mechanically treated to produce rough surfaces and cleaned by a supersonic wave instrument. Before electro-deposition, a number of substrates were pre-treated in 1 mole/litre sodium hydroxide solution at 80 °C for forty eight hours.

Calcium phosphate coatings were obtained by electrodeposition. The electrolyte was prepared by adding calcium nitrate tetrahydrate and ammonium hydrogen phosphate into distilled water. The pH value of the electrolyte was adjusted to 4.4 at 20 °C by the addition of hydrochloric acid. The electrolyte temperature was maintained at a constant (20 °C) by using an electric heater and magnetic agitation. The electrolyte temperature was monitored and controlled at 20 °C by a digital regulator with thermocouple. The current density was controlled at 10 mA/cm² for sixty minutes. Uniform and adherent coatings of calcium phosphate ceramic up to a certain thickness were obtained. Then a single hydroxyapatite phase coatings was prepared by hydrothermal treating specimens in an autoclave at 150 °C for four hours. The pH value of the solution was adjusted to be 12 with ammonia. Then the coated titanium cathodes were rinsed with distilled water and dried at room temperature in air. After the electro-deposited-hydrothermal synthesis, some specimens not pre-treated were calcined in air at different temperatures (600 °C, 700 °C, 800 °C and 900 °C) and pre-treated specimens were calcined in an argon atmosphere at 900 °C. These specimens with different process parameters were listed in Table 1.

X-ray diffraction (XRD, D/MAX-RA) was used to examine the phase compositions of calcium phosphate coatings and transition layers. The microstructures of the coatings and transition layers were studied by scanning electron microscopy (SEM, X-650). A transmission electron microscopy (TEM, H-800) was used to examine the crystal size of ceramic coatings. The bonding strength between the coating and the substrate was evaluated using a standard tensile adhesion test (ASTMC-633) for the electro-depositedhydrothermal synthetic coatings and coatings produced by calcination. Two identical cylindrical titanium substrates were used as a set. One rod was prepared with the coating. The coupling rod was glued with a thermoplastic and then joined under pressure in a fixture to the rod with the coating. The couples, cured at 180 °C for two hours, were subjected to tensile tests at an extension rate of 1 millimetre/minute until failure. For each test material, five specimens were used, and the bonding strength data in this study were the average values.

Results and Discussion

Phase compositions and microstructures of coatings

Fig. 1 shows the X-ray diffraction patterns of the various coatings. It has been shown that dicalcium phosphate dehydrate is the main phase of an electro-deposited coating (Fig. 1(a)), with peaks at 27.8°, 31.0° and 34.1°. The diffraction peaks of hydroxyapatite are also observed in the patterns. The following electrochemical reactions occur during the processes [15, 19]:

First, water is decomposed to hydrogen and hydroxide ions at the titanium substrate:



Fig. 1. X-ray diffraction patterns of the coatings. (a) electrodeposited; (b) hydrothermal treated; (c) calcination at 600 $^{\circ}$ C; (d) calcination at 700 $^{\circ}$ C; (e) calcination at 800 $^{\circ}$ C; (f) calcination at 900 $^{\circ}$ C.

Ta	bl	e	1.	Specimens	with	different	process	parameters
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specimens	pre-treated	Electro-deposition	hydrothermal treatment	calcination
1#	—	pH value 4.4, 20 °C	—	
$2^{\#}$	—	pH value 4.4, 20 °C	pH value 12, 150 °C, 4 h	
3#	—	pH value 4.4, 20 °C	pH value 12, 150 °C, 4 h	600 °C
$4^{\#}$	—	pH value 4.4, 20 °C	pH value 12, 150 °C, 4 h	700 °C
5#	—	pH value 4.4, 20 °C	pH value 12, 150 °C, 4 h	800 °C
6#	—	pH value 4.4, 20 °C	pH value 12, 150 °C, 4 h	900 °C
$7^{\#}$	1 M NaOH solution, 80 °C, 48 h	pH value 4.4, 20 °C	pH value 12, 150 °C, 4 h	900 °C

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$$2H_2O + 2e^- = H_2 + 2OH^-$$
(1)

Then, the generated hydroxide ions at the substrate surface react with dihydrogen phosphate:

$$OH^{-} + H_2PO_4^{-} = H_2O + HPO_4^{2-}$$
 (2)

The resultant HPO₄²⁻ ions combine with Ca²⁺ ions to form dicalcium phosphate dehydrate and dicalcium phosphate dehydrate deposits at the substrate surface:

$$Ca^{2+} + HPO_4^{2-} + 2H_2O = CaHPO_4 \cdot 2H_2O$$
 (3)

At the same time, with an increase in the density of hydroxide ions, a high pH value is beneficial to obtain hydroxyapatite. The chemical reaction is shown as follows:

$$6HPO_4^{2-} + (10 - x)Ca^{2+} + (8 - x)OH^{-} = Ca_{10-X}(HPO_4)_X(PO_4)_{6-X}(OH)_{2-X} + (6 - x)H_2O$$
(4)

Where x ranges from 0 to 2, giving a Ca/P atomic ratio between 1.67 to 1.33.

After the hydrothermal treatment, dicalcium phosphate dehydrate peaks disappear, and hydroxyapatite peaks intensify (Fig. 1(b)). The coating phase composition changes to a single hydroxyapatite phase. In the process, the pH value of the solution used for the hydrothermal treatment is very important in the dicalcium phosphate dehydrate-to-hydroxyapatite transition. When the pH value of the solution is above 12, the treatment time decreases to four hours and the treatment temperature decreases to 150 °C. The equilibrium is shown below:

$$(10 - x)CaHPO_4 + (12 - x)OH^- =$$
 (5)
 $Ca_{10-x}(HPO_4)_{x}(PO_4)_{6-x}(OH)_{2-x} + (4 - x)PO_4^{3-} + (10 - x)H_2O$

The finial coating phase composition is decided by the calcination process. When the temperature is below 700 °C, the coating phase composition remains a single hydroxyapatite phase (Fig. 1(c)). When the temperature is above 800 °C, the β calcium phosphate phase appears. The intensity and the number peaks of β calcium phosphate increase with an increase in the calcination temperature (Fig. 1(d), Fig. 1(e) and Fig. 1(f)). So the quantity of β calcium phosphate can be controlled by adjusting the calcination parameters. The chemical reaction is shown as follows:

$$Ca_{10-X}(HPO_4)_X(PO_4)_{6-X}(OH)_{2-X} = (1-x)Ca_{10} (PO_4)_6(OH)_2 + 3xCa_3PO_4 + xH_2O$$
(6)

Fig. 2 shows a scanning electron microscopy image of an electro-deposited coating. The calcium coating structure is porous. This coating can provide a large surface area to improve the osteological property. The non-oriented platelike phosphate crystals form an interlocking network with an average size of 150 nm, as shown in Fig. 3.

Fig. 4 shows a scanning electron microscopy image of



Fig. 2. scanning electron microscopy image of the electrodeposited coating.



Fig. 3. transmission electron microscopy micrograph of the electro-deposited coating powder.



Fig. 4. scanning electron microscopy image of the hydrothermal treated coating.

the hydrothermal treated coating. The crystals are needlelike and connect to each other in the coating. The size of the hydroxyapatite crystals remarkably decrease to 20 nm, as shown in Fig. 5.

Fig. 6 shows scanning electron microscopy images of the calcinated coatings. The microstructure of coatings does not change obviously when the calcination temperature changes. But the particles aggregate because of the loss of



Fig. 5. transmission electron microscopy micrograph of the hydrothermal treated coating powder.



Fig. 6. scanning electron microscopy images of the calcined coatings. (a) 800 °C; (b) 900 °C.

water (Fig. 6(a)). With an increase in the calcination temperature, a part of the hydroxyapatite changes to β calcium phosphate and the width and the length of β calcium phosphate crystal increases. Two distinct features can be seen in a scanning electron microscopy image (Fig. 6(b)). The small gray needle-like crystals are hydroxyapatite and the large white plate-like crystals are β calcium phosphate. These coatings can provide a relatively large surface area, which is particularly desirable for better chemical interaction with the biological environment.

Phase compositions and microstructures of transition layers

Fig. 7 shows the X-ray diffraction patterns of the transition layers. It is clearly seen that there are chemical reactions between the substrates and the atmosphere. For the specimens without a pre-treatment, after calcination below 700 °C in air, the transition layer can not be observed because the layers are too thin. When the calcination temperature is above 800 °C, the diffraction peaks of titanium nitride and titanium dioxide appear. The titanium substrate peaks are also observed because the transition layer is loose (Fig. 7(a) and Fig. 7(b)). For the pre-treated specimens, a thin and bioactive titanium dioxide layer is obtained. After calcining in an argon atmosphere at 900 °C, because oxygen and nitrogen can be avoided from the layer, the layer forms



Fig. 7. X-ray diffraction patterns of the transition layers after calcination. (a) 800 °C (in air); (b) 900 °C (in air); (c) 900 °C (pre-treated, in an argon atmosphere).



Fig. 8. scanning electron microscopy images of the transition layers after calcination. (a) 800 °C (in air); (b) 900 °C (in air); (c) 900 °C (pre-treated, in an argon atmosphere).

a dense and constant pure titanium dioxide transition layer.

Fig. 8 shows scanning electron microscopy images of the transitional layers. In the specimens without a pre-treatment, many cracks spread through the transition layers after calcination in air above 800 °C (Fig. 8(a) and Fig. 8(b)). These cracks sever the substrate and the coating, leading to an obvious decrease in the bonding strength. For pre-treated samples, a crack-free, homogeneous dense and constant pure titanium dioxide transition layer is obtained after calcination in an argon atmosphere at 900 °C (Fig. 8(c)). The existence of this layer increases the bonding strength remarkably.

Bonding strength between coating and substrate

The bonding strength is the most important factor that determines whether a calcium phosphate coating on a titanium substrate can be used in the human body or not. If the bonding strength is too low, the calcium phosphate



Fig. 9. bonding strengths between the calcium phosphate coatings and the titanium substrates.

coating is easy to shed from the substrate. Then the titanium substrate is exposed to the body liquid which leads to a surgery failure.

Fig. 9 shows the bonding strengths between the calcium phosphate coatings and the titanium substrates. It is clearly seen that the bonding strength of 7.66 MPa, is very low after the hydrothermal treatment. Calcination in air can improve the bonding strength when the temperature is below 700 °C. Above 800 °C, the bonding strength decreases obviously because of the appearance of a loose and thick titanium nitride and titanium dioxide transition layer. For the specimens pre-treated in a sodium hydroxide solution, a thin and bioactive titanium dioxide layer is obtained. Then a dense and constant pure titanium dioxide transition laver is created after calcination in an argon atmosphere at 900 °C. The bonding strength of these specimens is the highest, about 22.39 MPa, similar to of the coatings prepared by plasma spraying. This remarkable increase of bonding strength results from the existence of the titanium dioxide transition layer. The coefficient of thermal expansion of this layer is between the coefficient of thermal expansion of the substrate and that of the coating, leading to a reduction of the coefficient of thermal expansion mismatch between the substrate and the coating, which decreases the thermal stresses in the preparation process and reinforces the metallurgical combination. Furthermore, there is a favorable chemical affinity of titanium dioxide with respect to the hydroxyapatite coating and to the titanium substrate. So the tight bonding to the coating and the substrate also made an obvious contribution to the improvement in the bonding strength.

Conclusion

Hydroxyapatite/ β calcium phosphate coatings have been prepared in this study. The quantity of β calcium phosphate can be controlled by adjusting the calcination parameters. The coating has a porous structure, and can provide a large surface area to improve the osteological property.

For the specimens without a pre-treatment, the bonding strength is as low as 7.66 MPa after electro-deposited-hydrothermal synthesis. After calcining below 700 °C in air, the strength increases. However, because of the appearance of a loose and thick titanium nitride and titanium dioxide transition layer when the temperature is above 800 °C, the bonding strength decreases obviously.

For the pre-treated specimens, with a dense and constant pure titanium dioxide transition layer obtained after calcination in an argon atmosphere at 900 °C, the specimens have the highest bonding strength of 22.39 MPa.

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