General paper

Hydroxyapatite Coatings on Ti Plate via Chemical Bath Deposition

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Abstract: In recent years, the use of bioactive calcium phosphate coatings for biological fixation of load-bearing implants has been attracting much attention. Many techniques have been used to produce calcium phosphate, especially hydroxyapatite (HAP) coatings on metallic substrates. In this paper, a simple wet-chemical method, chemical bath deposition is reported to prepare calcium hydroxyapatite coatings on a Ti plate at relatively low temperature (95°C). The method is based on chelating calcium ions with a complex reagent and then increasing the temperature to dissociate the calcium ions, which induces the precipitation of HAP. EDTA is chosen as the complexing agent. At 60-95°C the Ca(EDTA)^{2-} complex thermally dissociates and releases free calcium ions. Substrates used in this research are Ti plates with 0.2 mm in thickness. The substrates were gritted by metallographic Al_2O_3 paper and then treated in a solution of 2mol/dm^3 KOH at 95°C for 1 hour. The HAP coatings were performed in a chemical bath that was heated from 60°C to 95°C. XRD data indicated that the coatings are highly crystalline. FTIR and EDX analyses revealed that the coatings consist of Ca-deficient apatite. SEM micrographs of the coatings show that the coating is composed of evenly small crystal grains. The surface was uniform without apparent pores or agglomerates.

Keywords: *Titanium, Hydroxyapatite, Coating, Chemical bath deposition, Implant materials*

1. INTRODUCTION

Hydroxyapatite (HAP), which is a main component of bone and tooth minerals, is currently used as biomaterial for many applications in both dentistry and orthopedics [1-2]. But its application is limited due to its poor mechanical properties [3-4]. On the other hand, titanium implants have been successfully used in clinics due to its excellent mechanical properties, chemical stability and good biocompatibility, which could be attributed to its surface oxide (TiO_2) film [5]. If HAP was applied as coating on a Ti substrate, both of the two implants' advantages would be properly combined.

At present, many techniques, such as sol-gel [6], plasma-spray [7-8], pulsed laser deposition [9-10], dipping method [11], thermal spraying [12], hot isostatic pressing [13], electrochemical deposition [14-15], have been proposed offering the potential for better control of the film structure. But the knowledge on bioactive mechanism, whether in experiment or theory, has been far from sufficient, and most of the methods are not satisfactory yet. Till present, only the technique of plasma spray has been so far used in clinics. However, problems encountered on coatings fabricated by the plasma spray methods are as follows: amorphous nature of coating, difficulties to coat odd-shaped objects, poor adhesion, and formation of other phases. Naturally, it is believed that an ideal bioactive method would be simple and cost-effective.

In this paper, in order to overcome all these shortcomings, a simple chemical bath deposition method was studied. The chemical composition of solution for deposition, heating process, and the effect of substrate on

the coating are discussed. The characterization of the synthesized HAP coatings was investigated.

2. EXPERIMENTAL PROCEDURE

2.1. Substrate Preparation

In the present research, the Ti plate was gritted with metallographic Al_2O_3 paper and then treated in a solution of 2mol/dm^3 KOH at 95°C for 1 hour. After that, it was washed with deionized water, and then dried.

2.2. Deposition Processing

The preparation of the chemical bath for deposition is shown in Fig.1. At first potassa was dissolved in deionized water; then EDTA was put in; ammonium dihydrogen phosphate was added next. At last calcium nitrate solution was introduced.

The substrates were vertically suspended in the chemical bath, which was heated in a water bath for deposition. The deposition was performed without stirring. After deposition, the substrates were taken out, washed with deionized water, and then dried.

2.3. Measurements

The surface morphologies were examined by scanning electron microscopy observations (S-4500, Hitachi, Japan), and the calcium to phosphorus ratio of the coatings was measured by an energy dispersive X-ray analysis (EDX). The crystalline structure and composition of the deposits scraped off from the substrate were analyzed by X-ray diffraction (XRD) using $\text{CuK}\alpha$

Fig.1. Preparation of the chemical bath solution

radiation. The Perkin Elmer System 1600 FTIR was used to study the chemical structure of the powders scraped off from the substrate. Pellet samples were prepared by mixing KBr powder with HAP to form thin transparent wafers.

3. RESULTS AND DISCUSSION

3.1. Chemical Control

Hydroxyapatite can be synthesized according to the following reaction:

In order to prepare the HAP coating on Ti plates, the reaction rate should be controlled. In chemical industry, a complexation agent has been widely used in order to control the reaction rate. The most commonly used complexation agent for calcium ions is EDTA (ethylenediaminetetraacetic acid). The solubility of EDTA in water is limited but can be increased apparently in alkaline solution. When the pH value is raised to 14, the EDTA is completely deprotonated. In the present research, potassium hydroxide has been utilized to dissolve the EDTA. After the EDTA has dissolved, ammonium dihydrogen phosphate is added, and then calcium nitrate solution is introduced. In these processes, some chemical reactions take place.

At first, EDTA reacts with potassium hydroxide:

When the calcium solution is put in, it reacts with potassium hydroxide at first:

Table 1 The composition of chemical bath solution.

Chemical agent	Amount
KOH	19g
EDTA	12.5g
$\text{NH}_4\text{H}_2\text{PO}_4$	3.17g
$\text{Ca}(\text{NO}_3)_2$	10g
Deionized water	100ml

Several minutes later, the precipitate disappears due to the reaction with EDTA to form a more stable structure:

The reaction of calcium complex and calcium ions is in dynamic equilibrium, which can be described as:

The stability constant value decreases with increasing temperature. That means, when the temperature of the chemical bath increases, the concentration of calcium ions increases according to reaction (5), which induces the reaction (1) to form HAP. Reactions (3), (4) and (5) suggest that the molar ratio of calcium salt and EDTA should be chosen as 1:1. If too much calcium salt was added, calcium hydroxide precipitate would be introduced, but when additional EDTA was used, the calcium ions would be very difficult to be released from the complexation structure.

In order to form HAP, the molar ratio of phosphate salt to calcium salt should be 3:5, which is given by reaction (1).

Much more potassium salt is needed in order to get deprotonated EDTA, which is the key problem for gaining HAP deposits.

The composition of the chemical solution used in the present research is shown in Table 1.

3.2. Substrates Pretreatment

Figure 2 shows the different morphology of the coating deposited on two different substrates. It is clear that the coating deposited on the as-received Ti plate is characterized by a relatively small grain size and some pores, while the one deposited on preliminarily treated Ti plate is even. The reason why may be as follows: the basic bath solution used in the present research dissolves the Ti plate and causes the evolution of H_2 , which results in the pores of the coating [16]:

In order to reduce the dissolution of Ti during the

deposition, it had been gritted and then treated with KOH solution at 95°C for 1 h before it was put in the chemical bath.

In the chemical bath for deposition, Ti-OH would attract Ca ions by Coulomb force, or combine phosphate ions in $\text{TiOH} \cdot \text{HPO}_4$ by covalent bonding [17], which would be benefit for the deposition of HAP and lead to much bigger grain size. So it is believed that the hydrated Ti layer would act as a bridge to improve the bonding strength of HAP coating to the Ti plate.

3.3. Heating Process

The deposition reaction starts at about 60°C. At that temperature the growing rate is quite low but it is accelerated with increasing temperature. As the water bath was used as a heater, the highest applicable temperature was limited to 95°C. If an oil bath or other

heaters are utilized, much higher temperatures would be obtained, i.e., much higher reaction rate can be reached.

But if we deposited the HAP at quite high temperature without previous heating process performed at relatively low temperature, high deposition rate results in homogenous nucleation. Most of the HAP precipitate would be lost and not grow on the substrate. So it is quite important to grow a thin layer of HAP at low deposition rate (by means of a low temperature). The existing HAP is used as a seed for the further deposition, which is an essential factor for the coating process. At the same time, the increasing rate of temperature should be slow especially in the high temperature range. The deposition was performed at 95°C for 3 h. Figure 3 illustrates the heating process of the deposition.

3.4. Characterization of the Synthesized HAP Coating

Figure 4 shows XRD pattern of the coating. Compared with HAP XRD standard (JCPDS 9-432), it is revealed that the coating is highly crystallized HAP.

Fig.2. Micrographs of the coatings deposited on different substrates: (a) as received Ti substrate, (b) the Ti substrate preliminarily treated with KOH.

Fig.3. The heating process of the deposition.

Fig.4. X-ray diffraction of the powder scraped off from substrate.

Fig.5. FTIR spectrum of the deposits scraped off from the substrate.

Figure 5 is a FTIR spectrum of the coating. The spectrum of the various phases were assigned (from literatures [18-20]) as follows: P-O peaks present at 559, 601, 960-1093 cm^{-1} , the peaks at 633 and 3572 cm^{-1} corresponds to O-H, the peak at 874 cm^{-1} belongs to P-O-H, and at 1418 and 1456 cm^{-1} the C-O absorption band is noticeable, indicating the $[\text{CO}_3]^{2-}$ group in the coating. It is well known that CO_2 can partially dissolve in water, and in basic solution its solubility increases. During the deposition process, CO_2 from the air dissolved into the bath solution and transformed to $[\text{CO}_3]^{2-}$, being incorporated into apatite by substitution of $[\text{PO}_4]^{3-}$ or OH^- . This is shown by reaction (7) and (8).

The achieved coating is Ca-deficient carbonate apatite, which is consistent with the EDX analysis. According to EDX analyses, the molar ratio of Ca/P was 1.57, lower than the 1.67 ratio in stoichiometric hydroapatite. In fact, biological apatite typically contains 5-8 wt% carbonate [21], so it is believed that the Ca-deficient carbonate apatite called as bone-like apatite [22] improves the level of biological response of the implant to the host in vivo [23]. It had been confirmed that the carbonate apatite have the potential of enhanced bioactive response when compared to non-carbonate apatite.

The morphology of the coating is shown in Fig.6. The surface is smooth without apparent pores. The thickness of the coating is about 6-8 μm , which can be roughly estimated by the cross section image. Higher thickness could be achieved by immersing the substrate

Fig.6. SEM micrographs of the coatings: (a) the surface of coatings, (b) the cross section of coating. S, substrate; C, coating.

into fresh bath solution and depositing for several times. The successive deposition can be started from 80°C.

4. CONCLUSIONS

In the present research, HAP had been evenly coated on whole titanium substrate by the chemical bath deposition method. The described method is very simple and easy to operate, which can be applied for fabrication of odd-shaped composite. Different with other wet chemical method, highly crystallized HAP coating was fabricated at quite low temperature — 95°C. Another notable merit of the present method is that the investment cost is quite cheap when compared with other methods, such as plasma spray method. The resultant coating was Ca-deficient carbonate apatite. The dense fracture-free coatings are promising implant materials because of its high bioactivity and mechanical strength.

Further research on mechanical and biological properties is needed in order to apply it in surgical operations.

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