A SIMPLE METHOD FOR PREPARATION OF HYDROXYAPATITE COATINGS

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Abstract: A novel, simple and economical chemical bath method for deposition of calcium hydroxyapatite coating has been developed. The coatings were prepared from EDTA solutions in alkaline media on Ti6Al4V substrates. The method is based on thermal dissociation of the $Ca(EDTA)^{2-}$ complex at 65-95 °C. Two chemical baths with and without presence of Na^+ and Cl^- were used for the deposition. The chemical bath A contained: $CaCl_2$, NaH_2PO_4, NaOH and sodium salt of EDTA, while the bath B consisted of: $Ca(NO_3)_2$, KH_2PO_4, KOH and EDTA. The Rutherford back scattering study shows that the coating material from bath A contains sodium and chlorine. The coatings prepared from bath B are characterized with the expected stoichiometry for HAP as well as molar ratio Ca/P = 1.67. The X-ray analysis revealed that the calcium hydroxyapatite coatings have preferred crystal orientation in the <002> direction.

Keywords: Calcium Hydroxyapatite, Coatings, Biomaterials

1. Introduction

Calcium hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, is the mineral component of bone which has attracted wide interest from both dental and orthopedic fields. Because of the frequent failure of the cemented implants, cementless implants coated with calcium hydroxyapatite have been suggested. A porous coating with ability to enhance the bone ingrowth over a gap that divides the implant surface from the tissue and improves fixation to the natural bone tissue improves the fixation and lifetime of the osteoconductive process.

Coatings of hydroxyapatite have been prepared by a variety of techniques, including sol-gel[1], plasma spray [2,3], rf sputtering [4], laser ablation method [5] and hydrothermal methods [6,7]. The problems associated with coatings prepared by rf sputtering are phosphorus deficiency and amorphous nature of the material. The latter causes fast resorption of the material by body fluids. The ion beam sputtering methods as well as a hot isostatic pressing methods have a problem with ability to coat odd-shaped objects. The electrophoretic methods have problems with poor adhesion and formation of other phases. Plasma spray has been the commercial method for preparation of calcium hydroxyapatite coatings. However this method suffers from formation of other phases like tricalcium phosphate, characterized with lack of crystallinity and poor adhesion to the substrate.

This paper describes an original chemical bath method for the deposition of oriented hydroxyapatite coatings. The chemical consideration, optimization of composition and temperature of the deposition solution are discussed.

2. Experimental procedure

2.1. Substrate preparation

Both as received and sandblasted Ti6Al4V pieces were used as substrates for the deposition. These substrates were treated in a solution of 2 mol/dm^3 KOH for one hour at 95 °C after sandblasting. The reasons for this treatment are described in detail in the chemical consideration section.

2.2.Coating deposition and characterization

The calcium hydroxyapatite coatings were prepared from two chemical baths. The stock solution for the chemical bath **A** was prepared by dissolving 50 g of EDTA sodium salt in 250 cm^3 solution of sodium hydroxide with concentration 2 mol/dm^3 in a beaker of 400 cm^3. When EDTA was dissolved 40 cm^3 of sodium dihydrogen phosphate with concentration of 3 mol/dm^3 and 40 cm^3 of calcium chloride with the same concentration were added. The stock solution for chemical bath **B** was prepared by dissolving 25 g EDTA in potassium hydroxide solution (35 g dissolved in 150 cm^3) in a beaker of 400 cm^3. In the prepared solution, 7.5 g of potassium dihydrogen phosphate were added. When the solid substance was dissolved, 50 cm^3 of calcium nitrate solution (19.5 g $Ca(NO_3)_2 \cdot 4H_2O$ dissolved in a 50 cm^3 water) were added. The chemical bath deposition was performed in 50 cm^3 beaker. The substrates were vertically suspended in the solution. The beaker was placed in a water bath. Heating of the chemical bath up to 65 °C for one hour was applied. After three hours at 80 °C, the temperature was increased slowly to 95 °C. After three hours deposition, the substrates were taken out, washed with water and dried. For obtaining thicker coatings the process was repeated with the same substrates, at 80 and 95 °C for several times. The deposition was performed without stirring in a water bath.

3. Results and Discussion

3.1. Identification and stoichiometry of the coating

A coating prepared by four successive depositions was used for X-ray analysis. The results indicate that the coated material is calcium hydroxyapatite characterized with preferred crystal orientation in the <002> direction.

The coatings from chemical bath **A** were characterized for their composition using Rutherford Back Scattering technique. The analysis revealed incorporation of Na^+ and Cl^- in the coatings that can be detrimental for the application. The composition of the material was simulated to be $Ca_{5.0}P_{3.3}O_{16}Cl_{0.3}Na_{0.8}$ (Ca/P = 1.515). Also surface carbon was detected on the coating using carbon resonance. In order to get stoichiometric calcium hydroxyapatite with Ca/P =1.67, chemical bath **B** was developed. Subsequent depositions in bath **B** resulted in coatings with desired composition. The spectrum corresponding to the stoichiometric calcium hydroxyapatite with Ca/P = 1.67, with composition confirmed as $Ca_{5.0}P_{3.0}O_{13}$ as well as carbon were detected in the material (not only on the surface as at coating prepared from chem. bath **A**) with amount of 0.7.

The sodium hydrogen phosphate is substituted with potassium hydrogen phosphate, sodium hydroxide is substituted with potassium hydroxide, calcium chloride is substituted

with calcium nitrate tetrahydrate and the sodium salt of ethylenediaminetetraacetic acid is substituted with the corresponding free acid. During the developing of the chemical bath **B**, efforts were made to make the bath close to the previous one with regards to sodium and chlorine content.

3.2. Optimization of the method

3.2.1. Optimization of the composition of the chemical solution

With varying the molar ratio of $Ca(NO_3)_2 \cdot 4H_2O$ and EDTA it was found that the maximum dissolved amount of $Ca(NO_3)_2 \cdot 4H_2O$ is always proportional to the equivalent amount of EDTA as it can be expected from the reaction (4). Any deposition made with a smaller molar ratio than 1: 0.89 of EDTA to $Ca(NO_3)_2 \cdot 4H_2O$ did not show any precipitate. If the deposition is performed with excess of $Ca(NO_3)_2 \cdot 4H_2O$ than there is calcium hydroxide suspended in the solution which is not desirable. Maintaining the molar ratio (~1:1) of EDTA to $Ca(NO_3)_2 \cdot 4H_2O$, the deposition temperature of 85 °C, and 2 hours deposition time, experiments with varying the mass of KH_2PO_4 and KOH in a solution with a volume of 40 cm^3 were performed. Fig. 5 shows the relation between the mass of the precipitate of HAP and mass of KH_2PO_4. As it can be seen, the optimal mass of KH_2PO_4 in a 40 cm^3 is around 1.5 g. The mass of KOH was also varied in the same volume from 2.34g to 8 g. It was found that the optimal mass of KOH is 7g.

3.2.2. Optimization of the deposition temperature

The optimized composition of the chemical bath was used for determination of the relation between temperature and coatings thickness. The deposition process was achieved with no stirring. It was noticed that the deposition reaction starts around 60 °C for the optimized composition. The growing rate at this temperature is low but might be essential for further faster growing of the coatings. Namely, if the reaction is performing at higher temperature with out previous deposition at temperature at 60-70 °C than the deposition rate will be low, the reaction rate will be very high and the main part of the precipitate will be lost with low gain in the thickness. The temperature was increased after reaching the saturation of the thickness. With increasing the temperature, the thickness also increases as a result of thermal dissociation of the calcium EDTA complex. High temperatures are desirable but not applicable by the water bath set up. The reaction performed at 70 °C ending for about 2 hours, at 80 °C ending for about 3 hours and for reaction performed at 95 °C ending for about the same, 3 hours.

The results of these studies indicated that the optimal precursors concentrations for deposition stock solution can be achieved by dissolving: 35 g KOH, 25 g EDTA, 7.5 g KH_2PO_4 and 19.5 g $Ca(NO_3)_2 \cdot 4H_2O$ in 200 cm^3 deionized water. The experiments conducted for determination of the optimal temperature shows that the temperature should be increasing from 65 to 95°C. The optimal time for deposition on 65 °C is one hour and is essential for the first deposition process. The optimal deposition time for 85 and 95 °C is 3 hours. From a single deposition can be prepared coatings with thickness of about 3 microns. Higher thickness was achieved by successive immersing of the substrate into fresh solution and the deposition can be started by heating at 85 °C. The growing rate on the existing coatings is much higher.

4. Conclusions

The described method is very simple and produces stoichiometric hydroxyapatite coatings with Ca/P =1.67. It can be applied for deposition onto complex-shaped implants. Note that the deposition temperature is below 100 °C with potential for deposition onto polymer substrates. The method was optimized by designed experiments to control the growth kinetics of stoichiometric HA coatings. The dense fractures - free coatings with preferentially oriented grains can improve adhesion with the substrate and also act as a barrier layer between implant surface and body fluids preventing the dissolution of the metal. These properties are appropriate for the initial layer in the by-layer HA coating designed to satisfy the essential requirements considering its application as a surgical implant material. The study of the deposition of the second very porous coating with thickness up to 100 microns for potential bone ingrowth thereby enhancing cementless fixation is reported [11].

Апстракт. Развиен е нов, едноставен и економичен метод на хемиска бања за депозиција на слоеви од калциум хидроксиапатит. Слоевите беа приготвени од раствори на EDTA во алкална средина врз супстрати од Ti6Al4V. Методот се темели на термичка дисоцијација на $Ca(EDTA)^{2-}$ комплексот изведена на температура од 65 до 95 °C. За хемиската депозиција беа користени две хемиски бањи. Бањата А содржеше: $CaCl_2$, NaH_2PO_4, NaOH и натриумова сол на EDTA. За разлика од неа, бањата Б се состоеше од: $Ca(NO_3)_2$, KH_2PO_4, KOH i EDTA. RBS анализите на слоевите приготвени од бањата А покажаа присуство на Na и Cl, а поради тоа и нарушена стехиометрија. Слоевите од калциум хидроксиапатит приготвени од бањата В се карактеризираа со ненарушена стехиометрија, како и молски однос Ca/P = 1,67. Рендгенската анализа покажа дека приготвените слоеви имаат преферирана ориентација во кристалографскиот правец <002>.

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