A simple chemical method for preparation of hydroxyapatite coatings on Ti6Al4V substrate

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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 Rutherford back scattering study shows that the coating material from bath which contained sodium and chlorine ions have their presence in the coated material. The bath which has been prepared with potassium substituting sodium and nitrate substituting chlorine produced coatings with better stoichiometry, with Ca/P = 1,67. The X-ray analysis revealed that the calcium hydroxyapatite coatings have preferred crystal orientation in the 002 direction.

1. Introduction

Calcium hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, is the mineral component of bone which has attracted wide interest from both the 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 r.f. 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 the 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 a unique chemical bath method for the deposition of oriented hydroxyapatite coatings. The chemistry consideration, optimization of composition and temperature of the deposition solution are discussed.

2. Experimental

2.1. Substrate preparation

Both as received and sandblasted Ti6A14V pieces were used as substrates for the deposition. These substrates were treated in a solution of 2 mol/dm^3 KOH for 1 h 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 1 h was applied. After 3 h at 80 °C, the temperature was increased slowly to 95 °C. After 3 h

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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 °C and 95 °C for several times. The deposition was performed without stirring in a water bath.

The XRD data were collected at an acceleration voltage and current of 50 KV and 30 mA, respectively on a Rigaku D/Max-IIB Diffractometer with CuKα radiation. A Tandetron, Genral Ionex and simulation using rump software was used for the RBS analysis. Surface profilometry was performed using Sloan Dektek II. A Mitutoyo Ultraplan FS-110 microscope with JVC TK 1280 U color video camera was used for the optical characterization.

3. Results and discussion

3.1. Chemical consideration

The idea for the chemical bath deposition method is based on a controlled performing of the following chemical reaction:

$$10Ca^{2+} + 6PO_4^{3-} + 2OH^- = Ca_{10}(PO_4)_6(OH)_2 \quad (1)$$

The reaction rate has been controlled by using a complexing agent. Ethylenediaminetetraacetic acid abbreviated as EDTA, has been used for complexing of calcium ions. EDTA sodium salt is the most widely used complexing reagent in volumetric analysis. The free acid is slightly soluble in water but very good in alkaline solution. Because of that, potassium hydroxide solution has been used to prepare the solution for chemical bath **B**. The dissolution process is a neutralization reaction and can be described with the following reaction:

$$H_4Y + 4KOH = Y^{4-} + K^+ + 4H_2O \quad (2)$$

where H_4Y is

$$\begin{matrix} HOOCCH_2 \\ {}^-OOCCH_2 \end{matrix} \diagdown\!\diagup NH^+ - CH2 - CH2 - NH^+ \diagup\!\diagdown \begin{matrix} CH_2COOH \\ CH_2COO^- \end{matrix}$$

and Y^{-4} is a deprotonated acid.

The reaction is exothermic and the solution warms up due to the liberated heat of neutralization. The pH value of the solution was 14. According to literature data [8] at that pH value, the EDTA is in completely deprotonated form into the prepared solution solid potassium dihydrogen phosphate was added. No visible changes were noticed. A white precipitate of calcium hydroxide has been observed when a calcium nitrate solution was introduced. After several minutes the precipitate has dissolved. The chemical reactions are given below:

$$Ca(NO_3)_2 + KOH = Ca(OH)_2 + 2KNO_3 \quad (3)$$

$$Ca(OH)_2 + Y^{4-} = CaY^{2-} + 2OH^- \quad (4)$$

The concentrations of the calcium complex as well as that of free Ca^{2-} ions are in dynamic equilibrium described by

$$Ca^{2+} + Y^{4-} \rightleftarrows CaY^{2-} \quad (5)$$

The reaction of precipitation of calcium hydroxyapatite can start only if the ions concentration is higher than the one defined by the solubility product. According to literature [9], the stability constant value decreases with increasing the temperature. This fact was used for increasing the concentration of free calcium ions. Namely, the equilibrium described with reaction (5) will be shifted to the left increasing the concentration.

Fig. 1(a) shows high concentration of cracks on the coatings deposited on substrates that were not treated with KOH. In order to prevent the cracking caused by the evolution of H_2 during the dissolution of the substrate (proceedings as shown in reaction (6) [10]) the substrates were treated with KOH to reduce the dissolution of Ti and Al during the deposition:

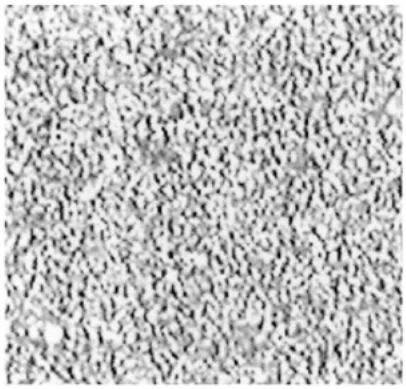
$$Ti + 4H_2O + nOH^- \longrightarrow Ti(OH)_{4+n}^{n-} + 2H_2 \quad (6)$$

Fig. 1(b) shows the dense crack-free surface of the coating on these treated substrates.

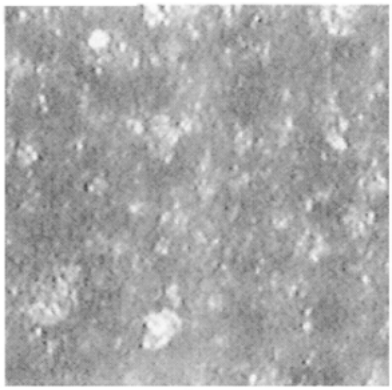
3.2. Identification and stoichiometry of the coating

A coating prepared by four successive depositions was used for X-ray analysis. Fig. 2 shows comparison of XRD pattern of the coating and calcium hydroxyapatite XRD standard (JCPDS 9-432). These 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 RBS. On Fig. 3 we observe incorporation of Na^+ and Cl^- in the coating that can be



a)



b)

Figure 1 Optical micrographs of hydroxyapatite coatings prepared from: (a) bath **A**, (b), bath **B**.

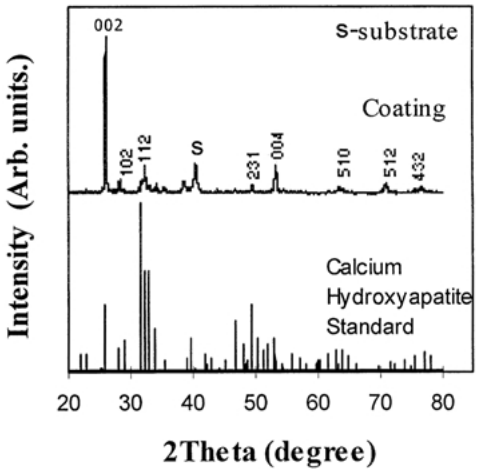


Figure 2 Comparison of X-ray diffractogram of coating with calcium hydrohyapatite standard.

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 (Fig. 4) 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.

As stated in the previous chemical discussion, 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.

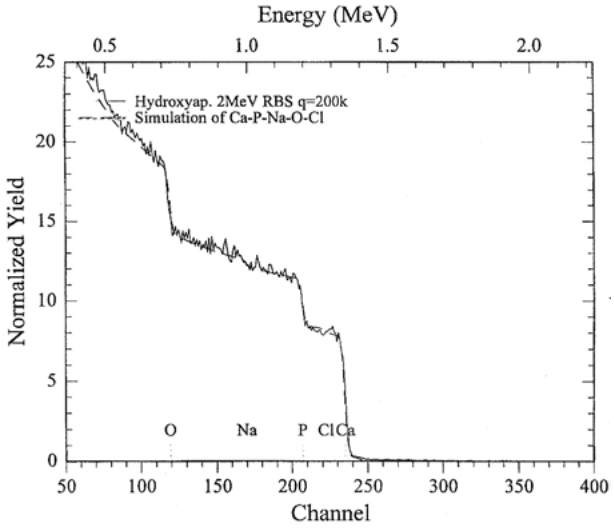


Figure 3 RBS spectra of hydroxyapatite coating prepared from bath **A**.

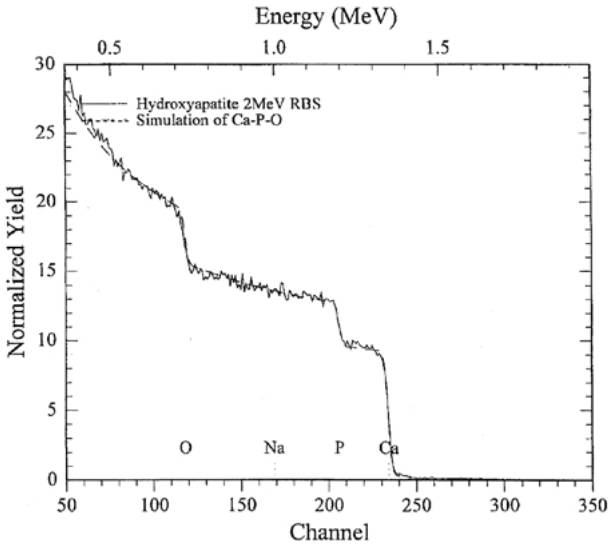


Figure 4 RBS spectra of hydroxyapatite coating prepared from bath **B**.

3.3. Optimization of the method

3.3.1. 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 ($\sim$ 1 : 1) of EDTA to $Ca(NO_3)_2 \cdot 4H_2O$, the deposition temperature of 85 °C, and 2 h 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 2.34 g to 8 g. The results are given in Table I.

It can be inferred from the table that the optimal mass of KOH is 7 g.

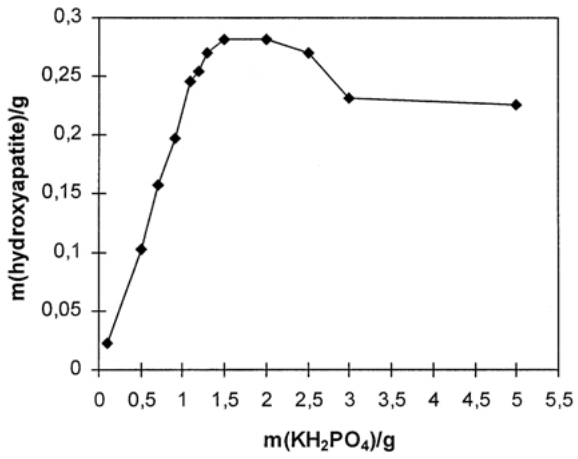


Figure 5 Mass of the precipitate of HAP versus mass of KH_2PO_4.

TABLE I Effect of KOH on mass of precipitate

KOH (g)	pH before deposition	pH after deposition	Mass of precipitate (g)
2.34	3.63	3.49	3.3827
4	4.99	4.78	0.2270
5	8.34	8.31	no ppt.
5.6	12.2	12	0.1788
6	13.3	13.2	0.2058
7	14	14	0.3255
8	14	14	0.2850

3.3.2. 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 results from the measurement of the thickness versus time at different temperatures are given in Fig. 6. 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. Fig. 6 indicate that the reaction performed at 70 °C ending for about 2 h, at 80 °C ending for about 3 h and for reaction performed at 95 °C ending for about the same, 3 h.

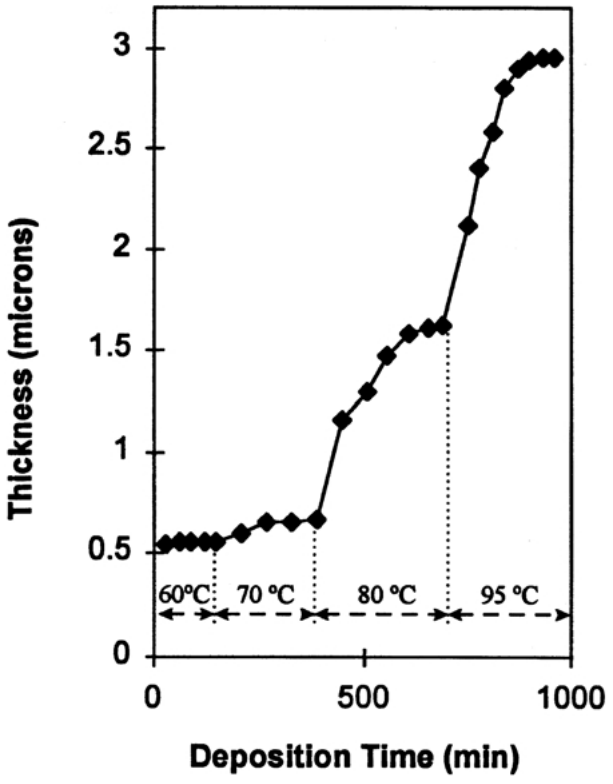


Figure 6 Plot of coating thickness versus deposition time at different temperatures.

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 °C to 95 °C. The optimal time for deposition on 65 °C is 1 h and is essential for the first deposition process. The optimal deposition time for 85 °C and 95 °C is 3 h. 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].

Acknowledgments

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