



Investigation of duty cycle effect on corrosion properties of electrodeposited calcium phosphate coatings

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ABSTRACT

The bioceramic calcium phosphate (CaP) is frequently used for improving bone fixation in titanium medical implants and thus increasing lifetime of the implant. It is known that the application of CaP coatings on metallic implant devices offers the possibility of combining the strength of the metals and the bioactivity of the ceramic materials. Many different techniques are available for producing CaP coatings. Electrochemical deposition method is widely used because of its ease of operation parameters, low temperature requirement, reproducibility and suitability for coating complex structures. This technique allows obtaining CaP coatings which promote bone in growth during the first healing period leading to permanent fixation. Electrochemical pulse technique is an alternative to calcium phosphate deposition techniques usually employed to cover orthopedic or dental titanium implant surfaces. Additionally, pulse electrodeposition technique can produce more uniform and denser CaP coatings on metallic implants. In this study, CaP based coatings were produced by electrochemical pulse technique on Ti6Al4V substrates. The resulting CaP deposits were investigated by means of X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). Corrosion properties of the CaP coatings were also investigated. The results showed that various duty cycle ranges have remarkably effect on morphology, crystallinity and corrosion properties of the produced CaP coatings.

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1. Introduction

Titanium (Ti) and its alloys are the most commonly used metallic materials for medical implants in orthopedic and dental applications, due to their low density, high strength, non-toxicity and excellent corrosion resistance [1]. In clinical usage, the coating should be biocompatible, show no toxicity effects, and provide a highly adhesive interface between bone tissue and the metallic implant. Additionally, the coating layer should also encourage bone tissue ingrowth and prevent the release of metal ions from the implant substrate [2]. Calcium phosphates (CaP) are primarily used as bone substitutes in biomedical industry due to their biocompatibility, chemical stability and their compositional similarity to the mineral phase of bone. Moreover, calcium phosphate coating is also an effective method to protect the implants from *in vivo* physiological environments as well as to provide bioactive surface which may promote the combination between bone and the implants [3]. Four types of CaP coatings have been achieved with electrochemical deposition (ED) method: brushite or dicalcium phosphate dehydrate (DCPD,

$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$), monetite or dicalcium phosphate anhydrous (DCPA, CaHPO_4), octacalcium phosphate (OCP, $\text{Ca}_8(\text{HPO}_4)_2(\text{PO}_4)_4 \cdot 5\text{H}_2\text{O}$), and hydroxyapatite (HAP, $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$). Although all of them exhibit excellent biocompatibility, it is reported that growth and dissolution of DCPD play an important role in the biological mineralization process as well as the setting of a variety of calcium phosphate cements for orthopedic and dental uses [4]. The reports about DCPD indicated that it is one of the precursors of HAP, which has similar mineral component as of the human bone. Initially formed DCPD coatings can be transformed into HAP through chemical methods [5,6]. Ducheyne and his colleagues reported that the phenomena of bioactivity, especially improvement of bone formation and bonding rates, is associated with dissolution of Ca^{2+} and PO_4^{3-} ions to implant-bone interface from the implant surface coatings [7,8]. In this case DCPD which is one of the soluble CaP phase can both enhance the HAP phase formation at implant-bone interface and increase ion concentrations, which require to Ca^{2+} and PO_4^{3-} for bone formation, by dissolving. Many methods are developed and used to prepare CaP coatings onto implant surfaces, for example, plasma spray, sol-gel, pulsed laser-deposition, electrophoretic method and electrochemical deposition [5]. The electrodeposition has not only the lower working temperature, but also can be used to deposit CaP coatings on any complex geometry substrates and it is a low cost process, so this technique attracts considerable attention due to the unique advantages [6,9].

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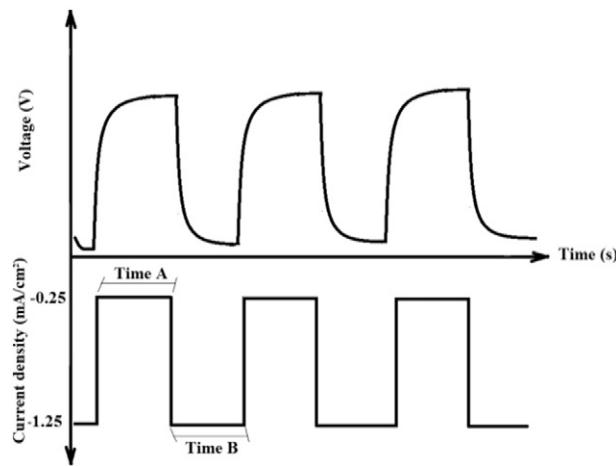


Fig. 1. Current-pulse profile imposed during the deposition of CaP based coatings.

Nevertheless, in a traditional cathodic electrodeposition process, when a static potential is applied, loose, porous and low adhesive coatings can easily develop. The main reasons are: first, a concentrations polarization is formed, since the speed of ion diffusion from the main body of the solution to the surface of the metallic substrate is too slow; and secondly, H₂ is produced in the cathode due to the reduction of H₂O [10]. Therefore pulsed electrodeposition (PED) can be used in order to optimize the material morphology and the composition. This technique is an advanced form of electrodeposition, which offers better control over deposit properties by controlling the interfacial supply and electrochemical reaction. Variables such as pulse waveform, cathodic/anodic pulses, on/off pulse time or duty cycle, applied potential, etc., offer effective ways to control macroscopic properties such as better adhesion, crack free hard deposits, fine grained films with higher uniformity and a lower porosity [11]. In pulsed electrodeposition technique plating currents are turned on and off in a controlled mode, resulting in a square wave with pulse duration, t_{on}, time between pulses, t_{off} and over all deposition duty cycle (Eq. (1)). PED has the advantage of flexibly creating complex alloy composition. By controlling metal ion concentrations, current density and pulse durations, nucleation of new crystals can be favoured over growth of existing crystals, resulting in films with ultra-fine grain structure [12]. The pulse power holds a relaxation time compared with the galvanostatic. In the electrodeposition process, as power is applied, the ions close to the cathode are adequately deposited. During the relaxation time, the ions can diffuse from bulk to the surface of cathode. In this process, both the concentration difference between the bulk and the surface of cathode and the polarization of concentration difference are reduced, so the physical-chemical properties of coatings can be improved [13].

$$\text{Dutycycle (DC)} = \frac{t_{\text{on}}}{t_{\text{on}} + t_{\text{off}}} \quad (1)$$

Table 1
Various reagents and compositions for preparing 1000 ml of SBF solution.

Order	Reagent	Composition
1	NaCl	8.035 g
2	NaHCO ₃	0.355 g
3	KCl	0.225 g
4	K ₂ HPO ₄ · 3H ₂ O	0.231 g
5	MgCl ₂ · 6H ₂ O	0.311 g
6	1.0 M HCl	39.0 ml
7	CaCl ₂	0.292 g
8	Na ₂ SO ₄	0.072 g
9	Tris	6.118 g
10	1.0 M HCl	0-5 ml

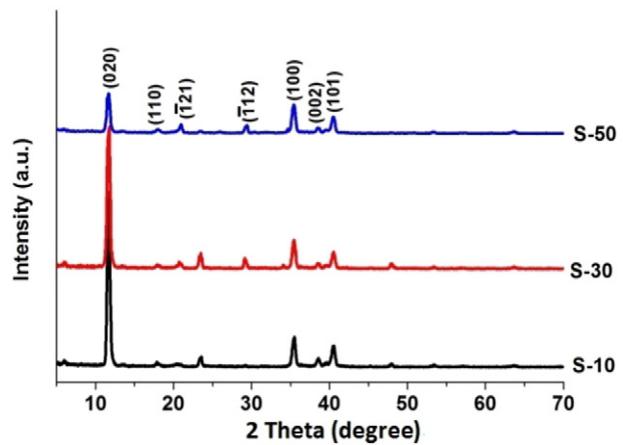


Fig. 2. XRD patterns of S-10, S-30 and S-50 coatings.

When ED method is used, H₂O is reduced into OH⁻, at the same time; a large amount of H₂ is produced. H₂ can severely prevent nucleating and growing of CaP on the surface of cathode, and produce the loose, porous and low adhesive coatings. On the other hand, the relaxation time between two deposition times (pulse cycle) strongly reduces H₂ bubbles emission and allows ions to diffuse from the solution to the cathode surface during the deposition process by using PED method. Moreover, the introduction of H₂O₂ into electrolyte reduces the voltage of cathode polarization and restrains the evolution of H₂ from the surface of substrate; therefore the adhesive strength between the coating and substrate is enhanced [13,14].

Aim of this study was to investigate effect of duty cycle on structure and corrosion properties of calcium phosphate coatings on Ti6Al4V substrates.

2. Experimental study

Ti6Al4V substrate was cut into discs with a diameter of 16 mm. All samples were grinded with SiC abrasive papers and polished with 3 μm diamond paste. After preparation, the samples were cleaned ultrasonically in deionized water/ethanol mixture for 10 min, and dried at room temperature. The electrochemical deposition of CaP coatings on Ti6Al4V substrates was conducted in the mixed solution of calcium nitrate tetrahydrate (Ca(NO₃)₂ · 4H₂O, Merck), ammonium dihydrogen phosphate (NH₄H₂PO₄, Merck) and distilled water. Additionally 2% hydrogen peroxide (H₂O₂) was added in electrolyte for depositing the adherent coating and NaOH added to adjust pH values to 4–5 [13,14]. The

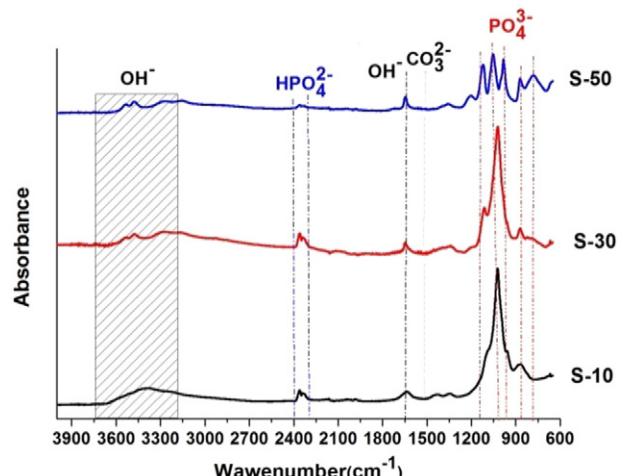


Fig. 3. FTIR spectra of S-10, S-30 and S-50 coatings.

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