Hydroxyapatite coatings electrodeposited at near-physiological conditions

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A B S T R A C T
Calcium phosphate (CaP) ceramics are used in orthopedics and dentistry due to their excellent biocompatibility and osseointegration. Plasma spraying has been the most common process for application of hydroxyapatite (HAp) coatings. Although electrodeposition (ED) has many potential advantages, very little has been published on ED of HAp at near-physiological conditions. Here we report the ED of uniform HAp–OCP (octacalcium phosphate) coatings on Ti–6Al–4V substrate at 37 °C, pH = 7.4, following surface pretreatment. Thermodynamic calculations were first used to predict which CaP phases may precipitate from solution under different experimental conditions. Microscopic observation revealed that the coating formed in this study is similar to that formed by chemical deposition, and better mimics the biological apatites in terms of structure and phase content than coatings currently used in orthopedics.

1. Introduction

Calcium phosphate (CaP) biocermics, especially hydroxyapatite (HAp, Ca5(PO4)3(OH)), have received much attention and have been clinically applied on orthopedic and dental implants due to their excellent biocompatibility and osseointegration. Various methods for applying CaP coatings have been reported in the literature, e.g. plasma spraying (PS), sputtering, sol–gel, chemical, etc. [1–5]. Currently, the most common method for applying such coatings on metallic substrates is PS [4]. However, great interest has evolved in recent years in electrochemical deposition (ED) due to its inherent advantages [5–15].

There is great interest in deposition of HAp and some other CaP phases such as octacalcium phosphate (OCP, Ca4(HPO4)(PO4)2·2.5H2O) at near-physiological conditions (in terms of both temperature and pH) and low applied current density or potential. If successful, such a process may allow incorporation of ingredients such as collagens, growth factors, peptides, bone-forming cells, and enzymes on one hand, and antibiotics on the other hand.

Nevertheless, most of the published procedures for ED of CaP (see, for example, Refs. [5–22] and Table 1) have involved relatively high deposition temperatures (aiming at improving the uniformity of the coating and the bonding between the coating and the substrate), high current densities, or non-physiological pH. For example, Kuo and Yen [18] demonstrated the formation of a uniform HAp coating on pure Ti substrate when using current densities higher than 10 mA/cm2. At lower current densities (1–5 mA/cm2), dibasic calcium phosphate dihydrate (DCPD, or brushite, CaHPO4·2H2O) was formed. Lopez-Heredia et al. [16] evaluated coatings that were formed at pH = 7.4 within a wide range of temperatures and current densities, including at near-physiological conditions. High temperatures were found necessary to obtain thick and uniform coatings. Rößler et al. [20] revealed growth of channels of CaP upon which spheres of amorphous calcium phosphate (ACP) formed under near-physiological conditions. ACP is a well-known precursor to HAp [11].

Neither of these past studies demonstrated good coatings formed under conditions suitable for incorporation of biological matter and drugs (namely, physiological temperature and pH combined with very low current densities). In this paper we report a one-step electrodeposition of uniform, well adhered HAp–OCP coatings on Ti–6Al–4V alloy at T = 37 °C, pH = 7.4, and low current densities (below 0.1 mA/cm2).

2. Materials and methods

A geochemical computer program (PHREEQC) was first used to determine the tendency of different CaP phases to precipitate from solution under different conditions of bath composition, pH and temperature. The principles and use of such thermodynamic
calculations have been demonstrated before [9]. The simulation results were subsequently verified experimentally.

A Ti-6Al–4V ELI grade rod was used as the substrate (working electrode). A series of surface pretreatments included mechanical grinding, surface activation in HF/HNO3 solution, grit blasting (GB), and soaking in 5 M NaOH at 60 °C for 24 h. Electrodeposition was carried out in a standard three-electrode cell in which two graphite rods were used as counter electrodes and a saturated calomel electrode (SCE) was used as the reference electrode. The electrolyte consisted of Ca(NO3)2 and (NH4)H2PO4. The solubility phase diagram of CaP was used as a starting point. Deposition conditions included pH = 7.4, T = 37 ± 0.1 °C, stirring at 200 rpm, applied potential of −1.4 V vs. SCE, and 2 h deposition time. The associated current density was fairly low, −0.1 mA/cm². More experimental details are provided elsewhere [6,7,12].

The surface morphology and the thickness of the coatings were characterized by environmental scanning electron microscopy (ESEM). X-ray diffraction (XRD) was used to determine the phase content. High-resolution X-ray photoelectron spectroscopy (XPS) measurements and analysis of the integrated intensities of the XRD patterns were subsequently used to calculate the O/Ca, Ca/P, and O(1s)/O(1s) ratios. High-resolution X-ray photoelectron spectroscopy (XPS) (ESEM). X-ray diffraction (XRD) was used to determine the phase and crystallographic information of the deposits. The coating was formed on a substrate with an oxygen-containing surface layer. The strength of adhesion of the HAp coating to the metal substrate was measured by a tension test, as described elsewhere in detail [15].

### 3. Results and discussion

**Table 1**

<table>
<thead>
<tr>
<th>pH</th>
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<tr>
<td>4.2 or 6.0</td>
<td>74</td>
<td>8–120 mA/cm²</td>
<td>Best coatings obtained above 70 °C</td>
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<td>25–80</td>
<td>72</td>
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<td>0–60</td>
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<td>36</td>
<td>6.4</td>
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<td>Deposited at 80 Torr. HAp formed at E ≥ 7 V, and its amount increased at 60 °C. HAp was always accompanied by DCPD or amorphous calcium phosphate (ACP).</td>
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<td>60</td>
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Fig. 1 shows the pH dependence of the saturation indices (SI) of HAp, OCP, DCPD, monetite (DCPA, CaHPO4), and tricalcium phosphate (TCP, Ca3(PO4)2), with respect to three bath compositions: (i) “Nominal”, 610 μM Ca(NO3)2 + 360 μM (NH4)H2PO4; (ii) “X0.1”, 61 μM Ca(NO3)2 + 36 μM (NH4)H2PO4; and (iii) “X10”, 6100 μM Ca(NO3)2 + 3600 μM (NH4)H2PO4. According to Fig. 1, for all three baths the solution is most supersaturated with respect to HAp throughout the whole pH range. The extent of supersaturation increases as the pH is raised. HAp is thus expected to precipitate spontaneously from solution over the whole pH range in all three cases. TCP may also precipitate from solution within most of the pH range. The extent of supersaturation extends to lower pH values (from 5.8 in Fig. 1a to 3.6 in Fig. 1c). At sufficiently high pH values, TCP may also form. The minimum pH value decreases from 9.2 in Fig. 1a to 5.4 in Fig. 1c. Although the initial pH in our experiments is 7.4, it is expected to rise in vicinity of the cathode during electrodeposition [12]. Based on Fig. 1, DCPD and DCPD will not form in solutions X0.1 and Nominal, no matter the pH is, and will have a very small driving force for precipitation in solution X10 within the pH range 5.2–10.

In order to better understand the role of different species in deposition at pH 7.4 and T=37 °C versus deposition at pH 6.0 and T=90 °C [9], Table 2 lists the activities of the different species in the Nominal solution. The activities of PO43−, HPO42−, CaPO42−, and CaH2PO42− are higher in the former case, while those of OH−, CaHPO4, and CaOH+ are lower. The effect of temperature is different from that of pH at a constant temperature of 90 °C, where increased pH resulted in increase in the activity of PO43−, OH−, CaPO42−, and CaOH+, and a decrease in the activity of CaH2PO42−. The main reactions for precipitation from solution of HAp and OCP are listed in Eqs. (1)–(5). From these equations it is evident that due to the aforementioned changes in the activities of different species, the likelihood of OCP formation is increased as the temperature is decreased from 90 °C to 37 °C while keeping the pH at 7.4.

**Table 2**

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Microscopic observation at low magnification revealed the coating that had been formed. As the coatings formed in solutions X0.1 and X10 were very thin, the focus here is on results for the Nominal solution only. Fig. 1d and e shows the typical surface morphology as evident by ESEM. The coating is fairly uniform and contains “mud-cracks”. Similar mud-cracks have been observed in carbonate apatite formed by sonoelectrodeposition, and were attributed to dehydration [23]. In our case, mud-cracks form already during the chemical pretreatment in NaOH [13]. Fig. 1d and e reveals the subsurface morphology of the coating. The surface morphology evident in Fig. 1d and e is significantly different from that of CaP electrodeposits formed before by Eliaz et al. at higher temperatures [7–10,12–14].

Metallurgical cross-sections (for example, see Fig. 2) revealed that the coating was 4.9 ± 2.4 μm thick (n = 16). Interestingly, the deposition rate is similar to that measured by Wang et al. [7] for a CaP coating electrodeposited from the Nominal bath composition at T = 85 °C and pH = 6.0. The effect of bath temperature on the electrodeposition of CaPs has been discussed by Eliaz et al. for other pH values [9,10]. It was found that the coating increases as the bath temperature is increased. In general, the dissociation constants of phosphoric acid, the density and dielectric constant of water, the A constant in the Debye–Hückel equation, the solubility products and the saturation indices of
different calcium phosphates are all temperature dependent. In addition, the OCP content increased as the bath pH was lowered from 6.0 to 4.2. The trends in the present study are opposite, indicating a synergistic effect of bath temperature and pH. The findings aforementioned imply that the mechanism of deposition must be different at $T = 37^\circ$C and pH = 7.4 versus $T = 85^\circ$C and pH = 6.0, as the different surface morphologies indicate.

XRD patterns (Fig. 3) revealed Ti reflections from the substrate along with HAp and OCP reflections. Energy dispersive spectroscopy (EDS) revealed a Ca/P atomic ratio of 1.85 ± 0.17, when excluding all other elements from the analysis. However, Eliaz et al. [11] have shown that EDS analysis is not reliable in identification of CaP phases, while advanced XPS analysis is effective. Indeed, advanced XPS measurements indicated that the coating consisted of 57% OCP and 43% HAp. The chemical composition of the coating is presented in Table 3. OCP is one of three phases that have been claimed to serve as precursors to the formation of HAp in vivo [11]. Furthermore, its presence in electrodeposited coatings and the related increase in the solubility of the coatings in vivo have been found to result in enhanced osseointegration [12]. The incorporation of OCP in the coating is likely to be beneficial in applications of controlled release of either antibiotics or incorporated biologic matter. Ti, Al and V from the substrate were not detected by XPS in this study, indicating that the coating is sufficiently thick.

The strength of adhesion of the coating to the metal substrate is one of the key factors determining the success or failure of the coating in vivo. International standards require that the value of the adhesion strength be at least 15 MPa [24,25]. The tensile stress to failure of the coating deposited in this study was $19.7 \pm 3.9$ MPa ($n = 3$). SEM-EDS analysis was used to determine the locus of failure; a cohesive failure (i.e. within the coating) was observed.
Thus, the coating deposited in this study meets the requirement of the FDA in terms of adhesion strength.

4. Conclusions

In this work, a well adhered, homogenous coating consisted of HAp and OCP was deposited electrochemically on Ti–6Al–4V ELI rods at near-physiological conditions ($T = 37^\circ C$, pH = 7.4). Thermo-dynamic calculations predicted the formation of HAp and OCP under these conditions. XRD and XPS analyses supported this prediction experimentally. While the surface morphology of the coating and the activities of different species in solution were found different from those of coatings electrodeposited at higher temperatures and lower pH values, the deposition rate was found similar, thus indicating that the mechanism of deposition may be different. The new coating may be loaded with both biological matter and antibiotics in order to further improve the osseointegration and infection resistance of future implants.

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References