



Electrocrystallization of nanocrystallite calcium phosphate coatings on titanium substrate at different current densities

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ABSTRACT

Calcium phosphates were electrocrystallized on titanium substrate by electrochemical deposition technique, in which the electrolyte was 0.167 M CaCl₂ and 0.1 M NH₄H₂PO₄. Different current densities (0.375, 1.5, 3, 6 mA/cm²) were applied. The pH of the solution after mixing of equal volumes was 4.6. The surface morphology, chemical composition and phase identification of the coatings were investigated by scanning electron microscopy associated with an energy dispersive spectrometer (SEM-EDXS) and X-ray diffractometry (XRD). Effects of the current density on the morphology and the structure of the coating were also discussed.

The results showed that at all current densities tested, the coating is brushite (dicalcium phosphate dihydrate CaHPO₄·2H₂O). Furthermore, the results showed that coating thickness and weight gain are increased and the morphology changed with increasing deposition current density (from 0.375 to 6 mA/cm²). On contrary, thickness and weight gain are decreased with sodium hydroxide treatment. NaOH treatment converts brushite of Ca/P ratio 1:1 to hydroxyapatite of Ca/P ratio of 1.667. So, chemical analysis of the solution shows soluble P₂O₅ content. Coating thickness at 6 mA/cm² was about 20 and 30 μm with and without treatment, respectively. It decreased to about 9.5 and 12 μm at 0.375 mA/cm² current density, with and without treatment, respectively. However, the formed phase is not changed with increasing current density. In addition, it is found that, even at high current density (6 mA/cm²), no hydroxyapatite was directly electrocrystallized due to low corresponding potential (less than 5 V) and low corresponding voltage (468 mV).

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1. Introduction

Calcium phosphates have received much attention and have been clinically applied in orthopaedics and dentistry due to their excellent biocompatibility. Among several forms of calcium phosphates, synthetic hydroxyapatite [Ca₁₀(PO₄)₆(OH)₂, hereafter HA], a major inorganic component of natural bone, is particularly attractive. HA is recognized as osteoconductive and able to accelerate bone in growth and attachment to the surface of implant during the early stages after implantation. Furthermore, the fixation and lifetime of the implant are improved. However, the mechanical strength is too poor to be used in load-bearing applications. Therefore, HA coatings on bioinert metallic prostheses were investigated to maintain biocompatibility and to improve mechanical properties [1–5]. Several methods have been reported to deposit HA onto implant surfaces, for example, plasma spraying, sputtering [6–12], pulsed laser deposition [13], sol–gel [14], electrophoretic method [15], and electrochemical deposition [16–18],

etc. Plasma spray method has been applied commercially for coating on titanium alloy implant surfaces. However, many issues remain concerning its use. This includes the presence of amorphous material and/or calcium phosphate crystalline phases other than HA such as Ca₂P₂O₇ and β-Ca₃(PO₄)₂ resulting from using extremely high temperatures in the plasma spray process [11]. Another issue of greater concern is the poor adhesion of the plasma-sprayed HA coating to titanium substrate due to the delamination of HA coating from the metal implant [12]. In addition, another problem cited with the plasma-sprayed coatings includes difficulty in microstructure control, which limits this approach in achieving optimum fixation with the implant.

Table 1
Specifications of HA coat

Property	Value	Property	Value
Thickness	Not specific	Heavy metals	<50 ppm
Crystallinity	62% min	Tensile strength	>50.8 MPa
Phase purity	95% min	Shear strength	>22 MPa
Ca/P ratio	1.67–1.76	Abrasion	Not specific
Density	2.98 g/cm ³		

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Table 2
Effect of coating parameters on formed phase of calcium phosphate

Current density/voltage	Materials	Ca/P ratio	pH	Tem., °C	Time, min	Phases	Ref.
2–10 mA/cm ²	0.042 M Ca(NO ₃) ₂ ·4H ₂ O 0.125 M NH ₄ H ₂ PO ₄	0.336	4.4	60	20	OCp, CadHA	[22]
1–5 mA/cm ²	0.042 M Ca(NO ₃) ₂ 0.025 M NH ₄ H ₂ PO ₄	1.68	4.5	60	30	B, OCP, TCP, HA	[23]
0.3–3.0 mA/cm ²	0.042 M Ca(NO ₃) ₂ ·4H ₂ O 0.025 M NH ₄ H ₂ PO ₄	1.68	4.76	65	16.7	MCPhn, MCP, B, OCP, HA	[24]
1–3 V	0.042 M Ca(NO ₃) ₂ 0.025 M NH ₄ H ₂ PO ₄	1.68	4.4	–	120	HA*	[25]
4–10 V	0.04 M Ca(H ₂ PO ₄) ₂ ·H ₂ O	0.5	3.0	0–60	60	B, TCP, HA	[26]
0.375–6 mA/cm ² 0.3–1.2 V	0.167 M CaCl ₂ 0.1 M NH ₄ H ₂ PO ₄	0.33 – 1.67	4.6	25	60–300	B, HA*	This paper

OCP: Octacalcium phosphate Ca₈H₂(PO₄)₆·5H₂O, CadHA: Calcium deficient Hydroxyapatite Ca₁₀(PO₄)₆(OH)₂, B (Brushite): Dicalcium phosphate dihydrate CaHPO₄·2H₂O, TCP: Tricalcium phosphate hydrate Ca₃(PO₄)₂·nH₂O, CaHPO₄·2H₂O, HA: Hydroxyapatite Ca₁₀(PO₄)₆(OH)₂, MCPhn: Monocalcium phosphonate monohydrate Ca(H₂PO₃)₂·H₂O, MCP: Monocalcium phosphate monohydrate Ca(H₂PO₄)·H₂O.

*After treatment with NaOH.

Calcium phosphate coatings have been deposited on metal substrates by electrochemical (electrocrystallization) method, which is an attractive process because highly irregular objects can be coated relatively quickly at low temperatures. Additionally, the thickness and chemical composition of coatings can be well controlled through adequate conditions of the process [2].

The specifications of HA coat (Table 1) have been described in the Food and Drug Administration guidelines as well as in the ISO standards [6,19,20].

Chu et al. [21] reported that new bone tissues can contact directly with Ti–40 vol.% HA graded as functionally graded biomaterial (FGB) at or after 4 weeks in vivo. After 8 weeks, the bonding interfaces between implant and new bones cannot already be distinguished and the implant was osseointegrated fully with bone tissues into one bony body.

Electrocrystallization method is relatively straightforward and the resulting coatings can be highly porous in nature. However, coating conditions can affect morphology, structure and coat phase [22–26]. Table 2 shows contradictions in some selected papers about type of electrodeposited phase. The main reason of contradictions is attributed to both current density and associated deposition voltage which affect phase formation.

HA, the most interesting form of calcium phosphates was electrochemically deposited in several solutions at elevated temperature and/or at high current density [12,24,26]. The coat deposited at room temperature and/or at low current density was brushite (CaHPO₄·2H₂O

DCPD) [12,24,26]. The formed dicalcium phosphate dihydrate (CaHPO₄·2H₂O, brushite, DCPD) can be easily converted to HA after soaking with sodium hydroxide solution at 80 °C for 2 h [18,25].

The novelty of this paper is doing electrodeposition at low voltage for the first time (less than 1 V) as well as different Ca/P ratio.

The coatings reported here were electrocrystallized at room temperature in CaCl₂ and NH₄H₂PO₄ aqueous solutions and treated with sodium hydroxide solution. The main objective of this paper is to understand coating properties as well as the formed calcium phosphate phase(s) on Ti substrate at different current densities.

2. Experimental procedure

2.1. Electrocrystallization of calcium phosphate on titanium

A single compartment electrochemical cell was used (Fig. 1) provided with a computer for recording the correlation between potential and time at each studied current density. Titanium sheets served as the cathode and were cut into disks of length 40 mm, width 10 mm and thickness 1 mm. After cutting, the specimens were homogeneously grinded with 600 grit SiC abrasive paper, etched for 5 min at room temperature. The etching solution consists of nitric acid (65%) 180 ml/l and hydrofluoric acid (42%) 23 ml/l in bi-distilled water. After rinsing with bi-distilled water, and ultrasonically cleaning with acetone for 5 min the specimens were air dried carefully and weighted. A platinum sheet of 4 cm² was serving as the anode. It was ultrasonically cleaned in acetone prior to use. A saturated calomel electrode (SCE) was used as the reference electrode along with a potentiostat/galvanostat instrument (Model PS6 Meinsberg, Germany) for electrochemical measurements.

The electrolyte solution used for the electrocrystallization of calcium phosphate consisted of 0.167 M concentration of CaCl₂ solution and 0.1 M concentration of NH₄H₂PO₄ solution. 150 ml of each solution was put into the cell while magnetic stirring. The Ca/P ratio in the mixed solution was equivalent to HA (1.67). The pH of the



Fig. 1. Electrochemical cell used in the tests.

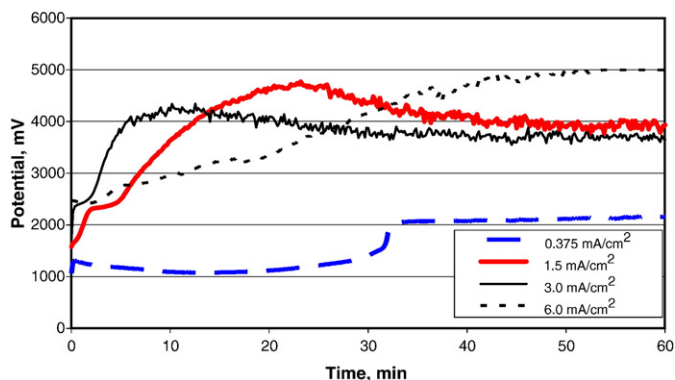


Fig. 2. Relation between potential and time at different current densities.

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