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Sol–gel derived hydroxyapatite coatings on titanium and its alloy Ti6Al4V

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Abstract

Titanium has been used for many medical and dental applications; however, its joining to a living bone is not satisfactorily good or the implant integration with bone tissue takes several months.The aim of this work is to produce hydroxyapatite (HAP) coatings on titanium and its alloy for facilitating and shortening the processes towards osseointegration. HAP coatings were obtained by sol–gel method with sol solutions prepared from calcium nitrate tetrahydrate and triammonium phosphate trihydrate as the calcium and phosphorous sources. Two types of gelatine were added to the sol: agar–agar or animals gelatine. Both were found to enhance the formation and stability of amorphous HAP using soluble salts as the sources of calcium and phosphate. HAP coatings were deposited from HAP–GEL sol using dip-withdrawal technique, then the plates were dried and annealed at temperatures 460–750 °C. FTIR spectroscopy and XRD analysis were used to study the phase composition of phosphate coatings. Morphology and chemical analysis of HAP layers was performed using a scanning electron microscope equipped with an energy dispersive X-ray analyser (SEM + EDX). The biological activity of sol–gel phosphate coatings was observed during thermostatic held in simulated body fluid (SBF). It was found that chemical composition and structure of HAP coatings depends on pH and final thermal treatment of the layer.

Keywords: Hydroxyapatite coatings; Sol–gel; Titanium substrates; Infrared spectroscopy

1. Introduction

The bioceramic hydroxyapatite Ca_{10} $[PO_4]_6[OH]_2$ (HAP) is frequently used as coat in titanium medical implants improving bone fixation and thus increasing a lifetime of the implant. It is known that the application of HAP coatings on metallic implant devices offers the possibility of combining the strength of the metals and the bioactivity of the ceramics [1–4]. Many different techniques have been used for the preparation of HAP coatings but plasma spraying is the most commonly used. However, at very high temperatures of the plasma, powder HAP particles at their surface may get into the molten state which undergoes the phase transitions forming the resorbable phases which degrade in a short period after implantation, decreasing the adhesion of the HAP layer to the bone as well as to the metal substrate [5].

The sol–gel method is an alternative means to form coatings and has several advantages: changing the chemistry or processing conditions can modify the microstructure of coatings. Additionally, sub-micron thin films of uniform thickness can be made using sol–gel techniques [6].

Bones and teeth are both composites principally comprised of hydroxyapatite and collagen. For a bone it is well established that formation of a collagen matrix precedes the deposition of hydroxyapatite. It is close synergy between the mineral phase and the organic matrix, which confers damage tolerance to bone [7,8].

Formation of a gelatine-containing composite has also been investigated as a model of mineralizing system. It was found that the presence of gelatine affects the kinetics of gypsum formation and microstructure of the gypsum that formed. Its presence may be inhibitory to reactions needed to form a mineral phase and it means that the presence of

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gelatine may affect the phase, which actually forms. For example, gelatine was found to enhance the formation and stability of amorphous calcium phosphate (hydroxyapatite) in precipitation reactions from salt solutions that would otherwise result in the formation of HAP [9–11].

The aim of presented work was to obtain apatite coatings from sols prepared from inorganic calcium and phosphorous salts with an addition of gelatine.

The hydroxyapatite sol was prepared using calcium nitrate tetrahydrate and triammonium phosphate trihydrate as the calcium and phosphorous sources. The quantities of the calcium and phosphorous were set to maintain a ratio 1.67–2.5. The reactions were performed at room temperatures in aqueous solutions at a pH from 6.0 to 7.8. Two types of commercial gelatine: agar–agar or animals gelatine were added to the sol. Both were found to enhance the formation and stability of amorphous HAP if soluble salts as the source of calcium and phosphate are used.

The sol was deposited on a titanium or titanium alloy plates with dip-withdrawal technique, then the plates were dried and heated at temperatures from 460 to 750 °C [12].

Evolution of the phase composition in the HAP layers obtained by sol–gel procedure was studied with the Fourier Transform Infrared Spectroscopy (FTIR). X-Ray diffraction (XRD) was used as a complementary technique. Morphology of HAP layers and chemical analysis was performed with scanning electron microscopy and X-ray microanalysis (SEM + EDS).

The biological activity of the coatings was observed during thermostatic held in simulated body fluid (SBF) [13].

2. Experimental

2.1. Materials and sol preparation

Titanium, pure, commercial (Goodfellow, GB), plates 15 × 20 mm.
Titanium alloy Ti6Al4V (Goodfellow, GB), plates 15 × 20 mm.
Calcium nitrate $Ca(NO_3)_2$. $4H_2O$, (AP grade). It was prepared 0.164 Mol/dcm^3 water solution.
Ammonium phosphate $(NH_4)_3PO_4.3H_2O$ (AP grade). It was prepared 0.098 Mol/dcm^3 water solution.
Ammonia: water solution (1:3).
Gelatine, commercial (from animals).
Agar, commercial agar gelatine.
Hydroxyapatite–gelatine (HAP–GEL) sol.
Simulated body fluid (SBF).

HAP–GEL sol was prepared by mixing a calcium nitrate solution with addition of gelatine and an ammonium phosphate solution. The proportions of the reactants were altered to obtain hydroxyapatite having the Ca/P ratios in the range 1.67–2.2. The reaction occurred at room temperature in aqueous solution at pH 6.0–7.8. The pH was adjusted with ammonia solution. Resulting colloidal sol was then mixed during 2 h with magnetic stirrer.

2.2. Coats deposition

Titanium plates, degreased and etched, were dipped in the HAP–GEL sol and withdrawn with the constant speed. Thickness of the forming deposit was controlled by multiple dipping. After the deposition was completed, the coats 'as-deposited' were carefully dried and annealed in argon at 460–750 °C. The heating removed water, densified the layer and improved its adhesion towards the substrate.

2.3. Analytical methods

The phase composition of coatings was analysed by FTIR reflection spectroscopy with Harrick Seagull attachment and by XRD analysis. It was used X-ray diffractometer X'Pert produced by Philips, with Cu Kα radiation, fixed angle setting 1/32°, Soller slits (0.04 rad) together with the scintillation detector and the flat crystal monochromator.

Morphology and chemical composition of coatings were analysed with scanning microscopy Philips XL 30 with X-Ray microanalyser Link ISIS-EDX.

3. Results and discussion

3.1. Agar–agar and gelatine characterisation

Since the agar–agar and gelatine were used for the preparation of HAP–GEL sols their phase analysis by FTIR spectroscopy, microchemical analysis and morphology by SEM + EDS were performed.

Agar–agar from plants is a natural gelatine $[(C_6H_{10}O_5)_n]$ with the structure of polysacharydes. Gelatine from animals is obtained by long time boiling (hydrolysis) of collagen from animal bones.

Fig. 1 shows the FTIR spectra of agar–agar (a) and gelatine (b) in the range of 400–4000 cm^{-1}. In Figs. 2 and 3 morphology and EDS analysis of agar–agar (Fig. 2a,b) and gelatine (Fig.3a,b) are shown.

Comparing the FTIR spectra in Fig. 1a,b, large differences are seen in the 1335–1538 cm^{-1} region, resulting from the presence of collagen in gelatine from bone. Differences are also observed in the chemical composition: agar–agar (Fig. 2b), apart carbon, contains also calcium and sulphur while gelatine (Fig. 3b) contains sulphur as a contamination. Morphology of agar–agar (Fig. 2a) looks like long, amorphous braids while gelatine powder (Fig. 3a) contains grains about 300–600 μm in diameter. Both type of gelatine gave satisfactory results but in our study we gave the preferences to agar–agar because agar–agar contained calcium that we believed to be more favorable when hydroxyapatite sol was formed.