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Electrochemical and morphological investigation of silver and zinc modified calcium phosphate bioceramic coatings on metallic implant materials

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ABSTRACT

In our research nanostructured silver and zinc doped calcium-phosphate (CaP) bioceramic coatings were prepared on commonly used orthopaedic implant materials (Ti6Al4V). The deposition process was carried out by the pulse current technique at 70 °C from electrolyte containing the appropriate amount of $Ca(NO_3)_2$ and $NH_4H_2PO_4$ components. During the electrochemical deposition Ag^+ and Zn^{2+} ions were introduced into the solution. The electrochemical behaviour and corrosion rate of the bioceramic coatings were investigated by potentiodynamic polarization and Electrochemical Impedance Spectroscopy (EIS) measurements in conventional Ringer's solution in a three electrode open cell. The coating came into contact with the electrolyte and corrosion occurred during immersion. In order to achieve antimicrobial properties, it is important to maintain a continuous release of silver ions into physiological media, while the bioactive CaP layer enhances the biocompatibility properties of the layer by fostering the bone cell growth. The role of Zn^{2+} is to shorten wound healing time. Morphology and composition of coatings were studied by Scanning Electron Microscopy, Transmission Electron Microscopy and Energy-dispersive X-ray spectroscopy. Differential thermal analyses (DTA) were performed to determine the thermal stability of the pure and modified CaP bioceramic coatings while the structure and phases of the layers were characterized by X-ray diffraction (XRD) measurements.

1. Introduction

Deep infection of megaprostheses is still a serious complication in orthopaedic surgery. The most commonly used implant material due to its excellent mechanical strength and chemical stability is the titanium alloy, Ti6Al4V [1–6]. However, bacterial adhesion and biofilm formation on these alloys can easily cause various human diseases after surgery [7].

Removing bacteria in a biofilm is impossible and a local or systemic antibiotic treatment is not effective. Therefore, the inhibition of bacterial adhesion is the most critical step in preventing implant-associated infections [8].

In view of the problem of bacterial resistance to antibiotics and antiseptics, nanostructured silver-containing coatings may be an effective way to prevent device related infections, because its high and permanent antimicrobial activity combines with a remarkably low human toxicity [9–10]. Silver and in particular the free silver ion is well known for its broad-spectrum antimicrobial activity and its low toxicity to mammalian cells, but still allows for the independent use of therapeutic antibiotics. Today the silver ions are used to control the bacterial growth in a wide range of medical applications, such as dental work, catheters, implant materials, wound healing and electrical appliances [8,11–12]. The antimicrobial success of silver comes from the fact that the silver cations (Ag^+) bind strongly to electron donor groups in biological molecules containing thiol (sulfydril, $-SH$) groups, oxygen and nitrogen [8]. Moreover, applying hydroxyapatite (HAp) coating improves the bioactivity of the titanium substrate and also acts as an interface for the transfer of biomechanical loading conditions from the implant to the surrounding bone tissues [13].

The role of zinc as a cationic substitution within hydroxyapatite is to counter the effects of osteoporosis. The zinc ion can affect the body and the skeleton in particular. Zinc is found in numerous enzymes and is known as a trace element in vertebrates. It has been demonstrated to have a wide variety of roles in various processes in the mammalian system, such as immune defence and wound healing. In particular, concerning bone metabolism, zinc stimulates bone formation in humans and many animals [14]. In most studies, zinc-substituted HAP and Zn-doped tricalcium phospates (Zn-TCP) were synthesized using zinc nitrate ($Zn(NO_3)_2$) and zinc acetate ($Zn(CH_3COO)_2\,2H_2O$) solutions as sources of zinc. It is also reported that the zinc calcium phosphate hydrate (parascholzite; $CaZn_2(PO_4)_2\,2H_2O$; ZCP) phase forms instead of zinc-substituted HAP and Zn-doped TCP when the zinc fraction is increased [15–18]. Parascholzite is generally more stable in an aqueous

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solution than HAP or zinc phosphate (hopeite; $Zn_3(PO_4)_2\,2H_2O$) [19,20] and is easily obtained by wet chemical methods. Horiuchi et al. reported developing novel zinc releasing bioceramics by incorporating zinc calcium phosphate into calcium phosphate cements by the wet chemical method [21]. Nowadays, many research groups are working on developing calcium phosphate based antimicrobial and biocompatible coatings on implant materials for biomedical applications. Commonly used methods are mainly Plasma Electrolytic Oxidation [22], Plasma Spraying [23–26], Pulsed Laser Deposition [27–29], Magnetron Sputtering [30, 31], Electrohydrodynamic Spraying [32], Spin Coating [33] Sol–Gel methods [34–36], Electrophoretic Deposition [37,38] and Electrochemical Deposition [39–48].

Current researches exhibit more interest on the pulsed electrodeposition of HAP coating as this technique possesses advantages including simple operation, high purity of deposits, easy control of the particle-size, compact coating and low cost.

In addition, geometrically complex implant surfaces can be coated with the ability to control the thickness, composition and microstructure of the deposits [42–44]. A smaller grain size of coating can be achieved on the metal substrate by PED method because it favours nuclei generation over grain growth [44,45]. The CaP coatings are not directly electroplated onto the substrate, instead, the reduction of water occurs at the surface of cathode. This reaction leads to a local increase in the pH at the electrode's surface to a level where the CaP becomes insoluble [45]. During PED, the concentration of the hydroxide ions (OH^-) produced at the substrate cathode affects the composition of the CaP. Deposition directly at higher pH favours HAp formation [46,47]. The performance of PED improves when H_2O_2 is introduced to electrolyte by reducing the voltage of the cathode polarization, which restricts the evolution of H_2 bubbles [43,48].

Many efforts are being made to develop modified calcium phosphate layers on implant materials in order to enhance their biocompatibility, however, to the best of our knowledge, none of them has dealt with the investigation of the effect of silver and zinc content on the corrosion and degradability properties of the modified calcium phosphate layers exposed to physiological solution for a long period of time, using Electrochemical Impedance Spectroscopy.

The aim of this study was to deposit nanostructured, modified (silver and zinc doped) CaP coatings by pulse current technology and to trace the corrosion properties of the pure and modified CaP coatings on metallic implants by electrochemical as well as to study the morphological changes in the coatings as-deposited and after soaking in physiological solution for two weeks.

2. Experimental and method

2.1. Preparation of pure and substituted hydroxyapatite coatings

Titanium alloy (Ti6Al4V, ISO5832-3, Protetim Ltd.) discs (19 mm × 1 mm) were used as substrates. One side of each disc was roughened using a sandblasting procedure with a 180-grit aluminium oxide media. The electrolyte used for the electrodeposition process of pure CaP bioceramic layer consists of 0.49 M $CaNO_3$, 0.29 M $NH_4H_2PO_4$ and 10 ml/l H_2O_2, while for deposition of modified hydroxyapatite layers, 10^{-3} M $AgNO_3$ and 10^{-3} M $ZnNO_3$ components were added to the base solution. The pH of the solution ranged between 4.0 and 4.5. For electrodeposition IGTV-4i/6 t type pulse current generator (BUTE, Hungary) was used to apply square waveforms at 500 Hz. The electrodeposition was carried out in a two-electrode cell under normal atmospheric conditions at a temperature of 70 °C, where the anode was a platinum sheet and the metallic implant disc was used as a cathode. The deposition parameters in all cases were 5 ms t_{on} and 5 ms t_{off} and current density of 400 mA cm^{-2}. During the deposition process the electrolyte was vigorously stirred. Applying t_{off} time in pulse current deposition gave the system time to recover during the zero current periods. The morphological changes of the layers were studied by SEM–EDX (Hitachi SU8230, Jeol 8230) and TEM (FEI Tecnai TF2).

2.2. Investigation of the thermal stability of the deposited layers

Differential thermal analysis and thermogravimetric (DTA/TGA) measurement were carried out using Setaram Setsys 16/18 apparatus (Setaram Company, France). The measurements were made at a temperature range from room temperature to 1100 °C at a linear heating rate of 10 °C/min in alumina crucible. High purity argon (Linde, 5.0) atmosphere was used to the experiment with 1.56 l/h flow rate. The measured masses of samples were 6 mg in all cases. As a reference an empty alumina crucible was used at the measurements. In all cases a background measurement was made with the same measuring parameters using blank alumina crucible. All measurements were corrected with the suitable background and then each curve was modified with the measured sample's mass. After this method the different measurements became comparable.

2.3. Structural characterization of the coatings

The crystal structures of the samples were investigated using X-ray diffraction. XRD spectra were recorded at room temperature by a Bruker AXS D8 Discover diffractometer (Cu K_α radiation source) equipped with Göbel mirror and GADDS 2D detector system operating at 40 kV and 40 mA. The diffraction patterns were collected over a 2θ range from 10° to 56° with an incremental step size of 0.05° using flat plane geometry.

2.4. Electrochemical evaluation of the coatings

The potentiodynamic polarization and electrochemical impedance spectra studies were carried out with Zahner IM6e electrochemical workstation (Zahner, Germany). In the electrochemical measurements conventional three-electrode cell was used. The working electrode was a metallic implant disc with and without coatings and platinum net and Ag/AgCl/KCl_{sat} electrodes were used as counter electrode and reference electrode, respectively. The potentiodynamic polarization curves were recorded with 1 mV/s scanning rate. Electrochemical impedance spectra measurements were carried out at open circuit potential of the working electrode at 35 °C by applying a 10 mV AC sine wave perturbation. A conventional Ringer's solution was used as an electrolyte for all the electrochemical experiments, which was prepared by adding (in) the AR grades 9.0 g/l NaCl, 0.43 g/l KCl, 0.20 g/l $NaHCO_3$, and 0.24 g/l $CaCl_2$ to the requisite quantity of distilled water, pH: 7.65. During the EIS measurements the frequency span was swept from 100 kHz (initial frequency) down to 10 mHz (final frequency). Impedance spectra were recorded several times during all measurements in order to trace the degradation of the coatings. Impedance spectra were represented in both complex impedance diagrams (Nyquist plot) as well as Bode amplitude and phase angle plots. In the Nyquist graph, the imaginary component of the impedance is plotted as a function of the real component, whereas the Bode representation shows the logarithm of the impedance modulus (|Z|) and phase angle (ϕ) as a function of the logarithm of the frequency (f). All impedance data were fitted and analyzed by using Zview (Scribner Associate, USA) software.

3. Results and discussion

3.1. Morphological investigation

Fig. 1 demonstrates the SEM/EDX measurements on substrate material (Fig. 1(a)), as well as pure and modified CaP coatings prepared by the electrodeposition method. It is clearly visible in Fig. 1(b) that the electrodeposited pure CaP coating has a mixture of small needle-like