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Radio frequency plasma treatments on titanium for enhancement of bioactivity

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Abstract

Titanium and its alloys, when treated in alkali solutions, are able to form calcium phosphate coatings on their surface after immersion in supersaturated solutions. In this study, the surfaces of titanium alloy discs were modified by an alkali treatment and a radio frequency (RF) plasma procedure (150 W and 13.56 MHz) in N_2, CO_2 or N_2/O_2 (80/20%) atmospheres. After the alkali treatment, atomic force microscopy showed differences in the surface roughness of the samples. X-ray photoelectron microscopy indicated that the chemical composition of the surfaces changed after the different alkali and RF plasma treatments. The contact angles were also modified by $\sim 5°$, making the original titanium surface more hydrophilic. Immersion in a supersaturated calcium phosphate solution was used to evaluate the bioactivity of the RF plasma-treated samples in vitro. Alkali-treated samples gave more homogeneous and thick coatings that those without alkali treatment. The use of RF plasma treatments enhanced the bioactivity of the samples, in particular for treatments performed in N_2 or N_2/O_2 atmospheres. Energy-dispersive X-ray analysis indicated that coatings had Ca/P ratios between the values of octacalcium phosphate and hydroxyapatite. X-ray diffraction confirmed the presence of these two phases in most of the coatings. This study shows that an RF plasma treatment enhanced the bioactivity of titanium surfaces.

Keywords: Titanium; Radio frequency plasma; Bioactivity; Calcium phosphate coating

1. Introduction

Titanium is mechanically and chemically suitable for use in orthopedic devices and dental implants, but lacks the bioactivity needed for bonding to bone tissue [1,2]. Different surface treatments have been developed to improve the bioactivity and osteconductivity of titanium implants [3,4]. For instance, osteoconductive calcium phosphate (CaP) coatings have been applied to titanium by several methods, such as plasma spraying, electrochemical methods and biomimetic precipitation [5–7]. The biomimetic method allows the deposition of CaP coatings on titanium surfaces after immersion of samples in simulated body fluids [7,8]. This ability to deposit CaP coatings on titanium is related to the physical and chemical properties of the surface [9,10]. Several physical, chemical and/or heat treatments have been used for the purpose of enhancing the precipitation of CaP, and hence the bioactivity of titanium implants [11]. Plasma treatments, such as energetic ion implantation, are well used to modify the surface tribological properties of titanium [12–15]. By using high-energy plasma, ions can be introduced into a titanium surface and/or coatings can be prepared by modifying the properties of the target surface [13,15–19]. Mandl et al. [20,21] used a plasma immersion ion implantation technique to create a rutile surface layer by introducing oxygen. They showed that this technique was capable of improving the biocompatibility and bone

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implant contact of the titanium-treated samples, as measured by a pull-out test of the implants from the site of implantation. Radio frequency (RF) plasma treatment is a low-temperature plasma technique that uses a high RF electric field between two electrodes to generate ionized gas plasma. RF plasma treatments modify the immediate surface region, i.e., less than 10–50 nm. We hypothesize that the RF plasma treatment may modify surface composition by introducing chemical groups on to the titanium, increase surface wettability and hence encourage the heterogeneous nucleation and growth of CaP crystals from supersaturated solutions. This surface modification may enhance the bioactivity of titanium implants both in vitro and in vivo.

The aim of this work was to study the effects of RF plasma treatments on the precipitation of CaP crystals by immersion in a supersaturated calcium phosphate solution (CPS). After alkali and RF plasma treatments in different atmospheres, the titanium surfaces were analyzed by means of scanning electron microscopy (SEM), atomic force microscopy (AFM), energy-dispersive X-ray analysis (EDX), X-ray diffraction (XRD) and X-ray photoelectron microscopy (XPS). Bioactivity was evaluated by measuring the uniformity of the coating, thickness and composition, and crystallinity after immersion in CPS.

2. Materials and methods

2.1. Titanium discs

Titanium alloy discs (Ti6Al4V, ALTA Industries, France), 15 mm in diameter and 1 mm thick, were machined from a bar for use in the experiments. The discs were ultrasonically cleaned in acetone, ethanol and demineralized water for 15 min and dried in a furnace at 90 °C overnight. Two groups of discs were used. The first group were treated chemically in 5 M NaOH for 24 h at 60 °C (TiNa) and for the second group no NaOH treatment was performed at all (Ti).

2.2. RF plasma treatments

After cleaning and NaOH treatments, two discs from each group were then subjected to an RF plasma treatment in a capacitively coupled plasma configuration (PM1820, Bronson, USA) in an N_2, CO_2 or N_2/O_2 (80/20%) atmosphere with operating conditions of 150 W, 13.56 MHz, 10 eV and 0.5 Torr for a period of 10 min. After this treatment, the sample temperature was approximately 100 °C. Two discs from each group received no RF plasma treatment at all for comparison purposes within their groups.

2.3. Calcium phosphate solution

The bioactivity of the treated titanium was measured by immersing the samples in CPS. The CPS solution was prepared by dissolving given amounts of NaCl (8 g), $CaCl_2 \cdot 2H_2O$ (0.59 g; 4 mM) and $Na_2HPO_4 \cdot 2H_2O$ (0.36 g; 2 mM) (VWR, France) in demineralized water and buffering at pH 7.4 with Tris(hydroxymethyl amino methane) (6.05 g, 50 mM) and drops of HCl 1 M. Each sample was immersed in 50 ml of CPS and kept in an incubator at 37 °C for 15 days. The solution was changed every 2 days. After immersion, samples were delicately rinsed with water and air-dried, before being characterized. The ability of the treated titanium surfaces to precipitate a CaP coating was determined by measuring the uniformity and thickness of the coatings.

2.4. Characterization of the surfaces

The surface roughness of the samples was measured using a mechanical profilometer (SJ-201M, Mitutoyo). Lengths of 0.8 mm were measured five times to obtain a sampling length of 4 mm. Surface roughness was measured three times on each sample. AFM was also used to characterize the microtopography of the samples with or without alkali treatment. AFM images were acquired in air using an Autoprobe CP Park Scientific Instrument (Sunnyvale, CA). AFM images were recorded using the tapping mode and conventional pyramidal silicon nitride cantilevers obtained from Digital Instruments (Santa Barbara, CA). All the tapping mode images (both amplitude and topography images) were acquired at a stable scanning force of around 100 nN. The contact angles (Digidrop, GBX) were measured in dynamic mode using demineralized water. After the RF treatments, three measurements were taken a few minutes apart for each sample. Contact angles were also measured after 24 h and 7 days for the different samples. The contact angle values did not differ significantly over time. The composition of the surface was analyzed with XPS (Leybold LHS 12) using an Mg source at 12 kV, 10 mA (120 W) and an operating pressure of 2×10^{-8} mbar. XPS was performed at the University of Nantes IMN-CNRS, and the data were analyzed with a SpecLab data system. SEM (Leo 1450VP), EDX (Oxford Instruments) and XRD (PW1830 Philips) were performed in order to characterize the composition and crystallinity of the titanium surfaces before and after immersion in CPS.

The uniformity of the CaP coatings was measured using back-scattered electron microscopy images and image processing software (Adobe Photoshop, Adobe Systems Inc.). The uniformity of the coating was determined from six images of each sample and expressed as a percentage. The thickness of the coatings was measured using the Eddy current method (Surfix, Phynix). Before measuring the thickness, the probe was calibrated by measuring a sample without coating and calibrated plastic films on this reference. The coating thickness was the average of five measures per sample.

3. Results

After alkali treatment, the Ti6Al4V discs turned green in color, with diffraction fringes indicating thickening of the