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Nanostructured Si-substituted hydroxyapatite coatings for biomedical applications

Julietta V. Rau ^{a,*}, Marco Fosca ^a, Ilaria Cacciotti ^b, Sara Laureti ^c, Alessandra Bianco ^b, Roberto Teghil ^d

^a Istituto di Struttura della Materia, Consiglio Nazionale delle Ricerche, Via del Fosso del Cavaliere, 100-00133 Rome, Italy

^b Università di Roma "Tor Vergata", Dipartimento di Ingegneria Industriale, UR INSTM "Roma Tor Vergata", Via del Politecnico, 1-00133 Rome, Italy

^c Istituto di Struttura della Materia, Consiglio Nazionale delle Ricerche, Via Salaria km 29.300-00016 Monterotondo Scalo (RM), Italy

^d Università della Basilicata, Dipartimento di Scienze, Via dell'Ateneo Lucano 10-85100, Potenza, Italy

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ABSTRACT

In the present work, the Si-HAP coatings were deposited on titanium substrates by Pulsed Laser Deposition technique. For deposition, the Si-HAP targets (1.4 wt.% of Si), produced starting from wet synthesized powders, were used. The properties of coatings were investigated by X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy, atomic force microscopy and Vickers microhardness. The obtained Si-HAP coatings presented a nanosized structure, proper thickness and hardness for applications in orthopedical and dental surgery, aimed at improving the stability and the osteointegration of bone implants.

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1. Introduction

During the last decades the demand for metal prostheses in bone surgery and dentistry is continuously and remarkably increasing [1,2]. In particular, titanium and its alloys are widely employed in the orthopedic and dental fields, due to the outstanding mechanical properties [3]. However, a fibrotic encapsulation is often formed around the titanium implants, affecting the long-term prosthesis stability. Moreover, titanium is unable to elicit a biologically functional bone/material interface. Therefore, the use of biocompatible surface coatings is aimed to improve the osteointegration of titanium-based implants.

In order to accomplish this objective, calcium phosphate materials are widely applied, presenting excellent biocompatibility and osteoconductivity. In particular, synthetic hydroxyapatite (HAP, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) has been extensively investigated as coating material for implants [4]. Various substitutions in the apatite lattice play a pivotal role in its biological activity, influencing solubility, surface chemistry and particle morphology of this material. Among the various ions, such as Na, Mg, Zn, Sr, Zn and Si, normally present in trace amounts (~1 wt.%) in biological apatites, silicon is considered to be essential for the extracellular matrix formation in bone and cartilage and to play a pivotal role at the early stages of bone mineralization and soft tissue development [5,6]. In many in vitro and in vivo studies [7–9], it was demonstrated that the Si incorporation into the HAP lattice induces a significant increase in the osteoblast cells activity and, consequently, decrease in bone opposition to the implant surface.

Currently, the plasma spraying is the only method commercially available for the HAP coating devices production [10,11]. However,

this technique presents many disadvantages, such as poor coating-substrate adhesion, voids and cracks formation, compositional variability and coating disuniformity in terms of both morphology and crystallinity. Consequently, the alternative coating methods, such as magnetron co-sputtering [12], sol-gel [13], aerosol deposition [14], electrolytic deposition [15], electrochemical deposition [16] and Pulse Laser Deposition (PLD) [17] have been developed to prepare the Si-HAP coatings. Among these deposition techniques, the PLD appears to be the most promising one, allowing to obtain films with the preserved stoichiometry of target material, to control the adherence, crystallinity and surface roughness. In our previous works, PLD was proved to be suitable for preparation of carbonate and fluorine-substituted HAP coatings [18,19].

On the basis of these previous results, in this paper the production and characterization of Si-substituted HAP coatings by PLD technique are reported. The main objective of this work was to optimize the deposition parameters in order to obtain good quality films, suitable for biomedical applications. For this purpose, the morphology, microstructure and mechanical properties of the deposited films were investigated by the X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM-EDS), Atomic Force Microscopy (AFM), and by Vickers microhardness.

2. Experimental section

2.1. Materials

2.1.1. Preparation of Si-HAP target

Silicon-substituted hydroxyapatite powder (Si-HAP) was prepared in a double-walled jacket reactor at 40 °C under continuous magnetic stirring, as reported in details elsewhere [20]. Briefly, the powder was synthesized by the titration of 10 g/l aqueous suspension of calcium

* Corresponding author. Tel.: +39 06 4993 4086; fax: +39 06 4993 4153.
E-mail address: giulietta.rau@ism.cnr.it (J.V. Rau).

hydroxide ($\text{Ca}(\text{OH})_2$, Aldrich 99.5%, MW 74.10) with a phosphoric acid solution (H_3PO_4 , Aldrich 86.3%, MW 98.00), using tetraethyl orthosilicate (TEOS) ($\text{Si}(\text{OC}_2\text{H}_5)_4$, Aldrich 99.99%, MW 208.33) as the silicon source. The TEOS was added to the phosphoric acid solution, prior to the titration with the calcium hydroxide suspension, in order to obtain a nominal composition in terms of Ca/(P + Si) ratio of 1.67 (Ca/P 1.82). The pH was finally adjusted to 9.4 by adding concentrated NH_4OH .

A silicon content of 1.4 wt.% was selected in this work, since it has been reported that Si results to be incorporated within the apatite lattice for amount lower than 1.6 wt.% [21] and that this content has proven a good biological response [9].

Precipitates were aged in mother liquor at room temperature for 24 h, washed with the NH_4OH aqueous solution, vacuum filtered and finally dried in oven at 60 °C (as-dried powder). After the pre-treatment at 600 °C for 1 h (heating and cooling rates of 10 °C/min), aimed to prevent the relevant weight losses during the densification process, on the basis of dilatometric data [20], the Si-HAp powder was uniaxially pressed at 400 MPa and sintered at 1100 °C for 1 h (heating and cooling rates of 10 °C/min). The actual Ca/P ratio of the obtained pellets (equal to 1.70) was evaluated by the Energy Dispersive X-ray Spectroscopy (EDS, INCA 300) microanalysis (detection limit 0.2%).

2.2. Methods

2.2.1. Pulsed laser deposition

The Si-HAp films were deposited on the heated Ti substrates in a high vacuum PLD chamber. Depositions were performed by ablating the sintered Si-HAp rotating target with a laser beam generated by a pulsed KrF Lambda Physik excimer-laser ($\lambda = 248$ nm). The laser pulse duration was 17 ns, and the repetition rate was 5 Hz. The laser beam was oriented with an inclination angle of 45° with respect to the target, whereas substrate and target were assembled in a frontal geometry at 4 cm of reciprocal distance. The PLD chamber was evacuated down to a pressure of 1×10^{-4} Pa prior to the film deposition; then, depositions were performed 5×10^{-2} Pa in a controlled dynamic pressure produced by the N_2 gas flow, introduced directly into the chamber through a needle valve. The deposition time was 25 min. The Si-HAp films were deposited at a fixed energy fluence of the laser beam (2 J/cm^2) and fixed temperature of the Ti substrate (600 °C).

2.2.2. X-ray diffraction

The Si-HAp target and films were analyzed using a *Panalytical X'Pert Pro* diffractometer (Bragg–Brentano geometry, $\text{CuK}\alpha$ radiation, $\lambda = 1.54184$ Å). The diffraction patterns were collected in an angular range of 20–90°. The Rietveld refinement procedure was possible only for the diffractogram of the target, being the intensity of the films' peaks too low, compared to those of the substrates. In this latter case only a qualitative search-match procedure with the PDF-2 database [22] was performed.

2.2.3. Fourier transform infrared spectroscopy

FTIR spectroscopy analysis was carried out, collecting a sequence of spectra by means of a *Jasco FT/IR 470 Plus interferometer* (Italy), equipped with an *IRTRON IRT-30* microscope. Each spectrum was acquired in the reflectance mode by executing 250 scans at 8 cm^{-1} resolution, in the range of 4000–550 cm^{-1} .

2.2.4. Scanning electron microscopy

SEM apparatus (*LEO 1450 Variable Pressure*), working in the secondary and backscattered electron modes, with the resolution of about 4 nm in vacuum conditions, was utilized for morphological studies of the deposited coatings. This SEM apparatus is coupled with a system for microanalysis EDS (Energy-Dispersive X-ray Spectroscopy) *INCA 300* that allows executing qualitative/quantitative analysis of the elements with the precision limit of about 0.2%.

2.2.5. Atomic force microscopy

A non-commercial atomic force microscope was used to investigate the surface texture of the deposited films. At first, several portions of the samples were observed, collecting the $10 \times 10 \mu\text{m}$ images, in order to evaluate the homogeneity of the film growth. Subsequently, the high resolution images ($5 \times 5 \mu\text{m}$, 400 points/line) were acquired to obtain the quantitative information about the surface fine topography.

2.2.6. Vickers microhardness

The microhardness measurements were carried out by means of a *Leica VMHT* apparatus (*Leica GmbH*, Germany), equipped with a standard Vickers pyramidal indenter (square-based diamond pyramid of 136° face angle). Six loads, ranging from 0.49 up to 9.8 N, were applied for 15 s at loading and unloading speed of 5×10^{-6} m/s. For better statistics, approximately 10–15 indentations were performed at each load. Hardness of the Ti substrate and of the deposited film was measured according to the procedure described in detail in our previous works [18,19].

For the Ti substrate, the hardness measured in a separate experiment equals to 1.8 ± 0.1 GPa.

For the film, the measured hardness is that of the film/substrate composite system. To extract the film hardness from the composite film/substrate hardness, a Jönsson and Hogmark “law-of-mixtures” model was applied [23].

3. Results and discussion

The synthesized Si-HAp powder was composed of semicrystalline, high specific surface area (i.e. $84 \text{ m}^2/\text{g}$), nano-sized needle-like (10–20 nm wide and 50–200 nm long) particles, consisting of thermally stable (up to 1200 °C) monophasic HAp [20]. The produced target was characterized by a densified and residual porosity-free surface. The diffractogram of the Si-HAp target clearly shows the fingerprint pattern of hydroxyapatite (card number 84-1998 [22]) (Fig. 1A), since the 1.4 wt.% Si amount does not significantly affect the crystal lattice of hydroxyapatite.

In the diffraction pattern of the deposited film (Fig. 1B), the dominating peaks are those of the Ti substrate (Ti (100), Ti(002), Ti(101), card number 44-1294 [22]). This result is typical for X-ray diffraction spectra of thin films [18,19]. Nevertheless, also the film's reflections can be well distinguished, such as the HAp most intense reflection (HA (121), 100% intensity, card number 84-1998 [22]) and a peak attributable to CaO ((222), card number 86-1585 [22]), suggesting partial HAp decomposition. The average crystallite size, of about 36 ± 1 nm, was estimated applying the Scherrer equation. The obtained value demonstrates that the deposited coating is nanostructured.

To further investigate the properties of the prepared crystalline film, the FTIR analysis was performed. The FTIR spectra of the Si-HAp target and of the film are shown in Fig. 2. As can be observed, the graphs are characterized by the presence of a typical HAp broad absorption band of a comparable intensity at around 1100–900 cm^{-1} . According to the literature data [20], it can be attributed to the phosphate bands (PO_4^{3-} stretching vibration mode). It has to be pointed out that SiO_4^{4-} and PO_4^{3-} tetrahedral molecular units share many of similarly spaced vibration modes in the 1100–900 cm^{-1} region, such as: 1089–1095 cm^{-1} (Si–O/P–O stretching), 1020 cm^{-1} (vibration mode of PO_4^{3-} -group/Si–OH deformation vibration) and 958–962 cm^{-1} (Si–O/P–O symmetric stretching) [20].

The film's morphology was investigated by SEM. The plane view SEM micrograph of the coating at 1000× magnification is presented in Fig. 3, showing dense, compact and granulated surface. From the cross-section SEM image, the average film thickness was measured and equaled to $1.5 \pm 0.2 \mu\text{m}$.

The qualitative investigation of the elemental composition of the prepared coating, in terms of Ca/P atomic ratio and Si content, was carried out by means of the SEM–EDS analysis. The deposited film is

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