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Pulsed laser deposition of strontium-substituted hydroxyapatite coatings

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ABSTRACT

The growing evidence of the beneficial role of strontium in bone has increased the interest of developing strontium-containing biomaterials for medical applications, and specifically biocompatible coatings that can be deposited on metallic implants to benefit from their load-bearing capabilities. In this work, strontium-substituted hydroxyapatite (Sr-HA) coatings have been fabricated by pulsed laser deposition (PLD) from initial targets obtained after mixing and compacting commercial HA and $SrCO_3$ powders in different proportions. The films thus fabricated were then structurally, morphologically and chemically characterized using scanning electron microscopy, optical profilometry, X-ray diffraction, Fourier-transform infrared spectroscopy, X-ray photoelectron spectroscopy and energy dispersive X-ray spectroscopy. The macroscopic morphology of the films presented in all cases equivalent spherical shaped aggregates of typical calcium phosphate coatings. The results reveal, however, the incorporation of Sr^{2+} and carbonate groups in the coatings as a function of the $SrCO_3$ content in the ablation target, being the incorporation of Sr^{2+} a linear phenomenon that is accompanied by a similarly linear withdrawal of Ca^{2+}. The role of Sr^{2+} in the modification of the HA structure and a possible mechanism of substitution of Sr^{2+} atoms in place of Ca^{2+} atoms are discussed.

1. Introduction

Hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ (HA) is a member of the mineral family of apatites used extensively as a biomaterial due to its resemblance to the inorganic phase of bone. As a coating of metallic implants, one of its most common applications, it avoids the release of metal ions into the body and improves the implant fixation to hard tissues [1]. However, there is still room for the enhancement of this osteointegration process, potentially reducing post-operatory recovery and long term failure. Hydroxyapatite presents the property of being able to incorporate a variety of ions and compounds into its structure [2], and indeed the natural hydroxyapatite present in bone contains different elements that have proven to play an important role in bone formation and normal functions of bone tissue [3]. Among these, some relatively abundant ions are Mg^{+2}, K^+, Na^+ and F^-, as well as the compound ${CO_3}^{2-}$, their biological role and incorporation mechanisms having already been studied [4–8]. However, other elements present at very low concentrations have only recently been shown to play a vital role in the development of the skeleton. One of these is Sr^{2+}, that tends to substitute Ca^{+2} by ionic exchange in the hydroxyapatite structure due to their similar chemical characteristics, and that has been shown to be present at higher concentrations in the regions of high metabolic turnover of bone [9]. Although first regarded as toxic due to its negative effects at high dosage [10], the role of Sr^{2+} as an important element in the biology of the skeleton started to become clear in the last two decades with the study of the effect of Sr^{2+} administration in osteoporotic patients. In particular, the proven effectiveness of the drug strontium ranelate to treat this illness has been a turning point in this research [11]. Studies *in vitro* have shown that the presence of Sr^{2+} results in an increase in the number of osteoblasts and a reduction in the number and activity of osteoclast cells [12], while *in vivo* studies have shown an improvement in bone formation and a reduction of bone resorption [13]. As a consequence, Sr^{2+} is now regarded as a potential enhancer of bone implants.

Several studies have been performed to obtain strontium substituted apatites as a filler material and as a coating. Strontium substituted hydroxyapatite (Sr-HA) coatings have been successfully obtained with several methods, such as biomimetic precipitation and plasma spray deposition [14,15]. Pulsed laser deposition (PLD) is a technique that has proven effective in the fabrication of calcium phosphate films on metallic substrates with excellent final coating attachment [16]. It makes use of laser pulses to expel target material from a rotating disk placed inside a reaction chamber and project it on the surface of a metallic substrate. The PLD method outperforms other techniques in versatility, since the choice of its ablation and deposition parameters allows the control of the stoichiometry and crystallinity of the deposited material [17].

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This technique has only very recently started to be studied in the fabrication of Sr-HA coatings, showing a good response in *in vitro* experiments [18]. In this paper we present a processing method by PLD to obtain Sr-HA coatings in a more simple way, from a starting material consisting of mixed and compacted HA and $SrCO_3$ powders, avoiding the need to chemically synthesize the strontium apatite before its deposition, and incorporating $CO_3{}^{2-}$ compounds into the apatite structure in the same processing.

Table 1
Designation of the samples, both targets and coatings, with the atomic percentage of Sr in the former ones.

Target	at.% Sr	Coating
HA ref	0	RHA
Sr2.5	2.5	RSr2.5
Sr5.0	5.0	RSr5.0
Sr7.5	7.5	RSr7.5
Sr10.0	10.0	RSr10.0

2. Materials and methods

PLD Sr-HA target disks with a mass of 2 g and a diameter of 20 mm were fabricated with the homogeneous mixture of commercial carbonated HA and $SrCO_3$ powders and the subsequent application of pressure (30 MPa) without the use of any calcinations or sintering processes as described in [19,20]. Five targets with different concentrations of strontium were fabricated, containing 0, 2.5, 5.0, 7.5 and 10.0 at.% Sr^{2+} and labeled HA, Sr2.5, Sr5.0, Sr7.5 and Sr10.0, respectively (Table 1). The coatings then produced with the laser ablation of these targets were labeled RHA, RSr2.5, RSr5.0, RSr7.5 and RSr10.0. The deposition was carried out on rectangular-shaped Ti and Si substrates previously submitted to a cleaning protocol. The films were pulsed laser deposited using a UV ArF excimer laser source ($\lambda = 193$ nm). The target material was irradiated for 15 min with a pulse frequency of 10 Hz and an energy density of 3.2 J cm^{-2}. Previous to the deposition, the chamber atmosphere was evacuated down to a pressure of 10^{-5} mbar and subsequently filled with a water vapor atmosphere of 45 Pa. The substrates were maintained at a temperature of 460 °C. These deposition parameters were optimized in previous research works [16,19,20].

The morphology of the coatings was analyzed by scanning electron microscopy (SEM) using a JEOL JSM-6700F microscope and by optical profilometry using a Wyko interferometric NT 1100 microscope. Structural and compositional measurements were taken by X-ray diffraction (XRD), Fourier transform spectroscopy (FTIR), energy dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS). The XRD analysis was performed with a Siemens D5000 diffractometer using Cu Kα radiation and a grazing angle of 0.5°. FTIR was carried out with a Bomem MB-100 spectrometer in the range of 550–5000 cm^{-1}, and a $CO_3{}^{2-}/PO_4{}^{3-}$ ratio of peak areas was used to avoid the influence of the films thickness in the quantification analysis. For XPS, a K-ALPHA spectrometer using monochromatic Al Kα ($h\nu = 1486.92$ eV) radiation was employed. Finally, EDS analyses were carried out with an Oxford Inca Energy

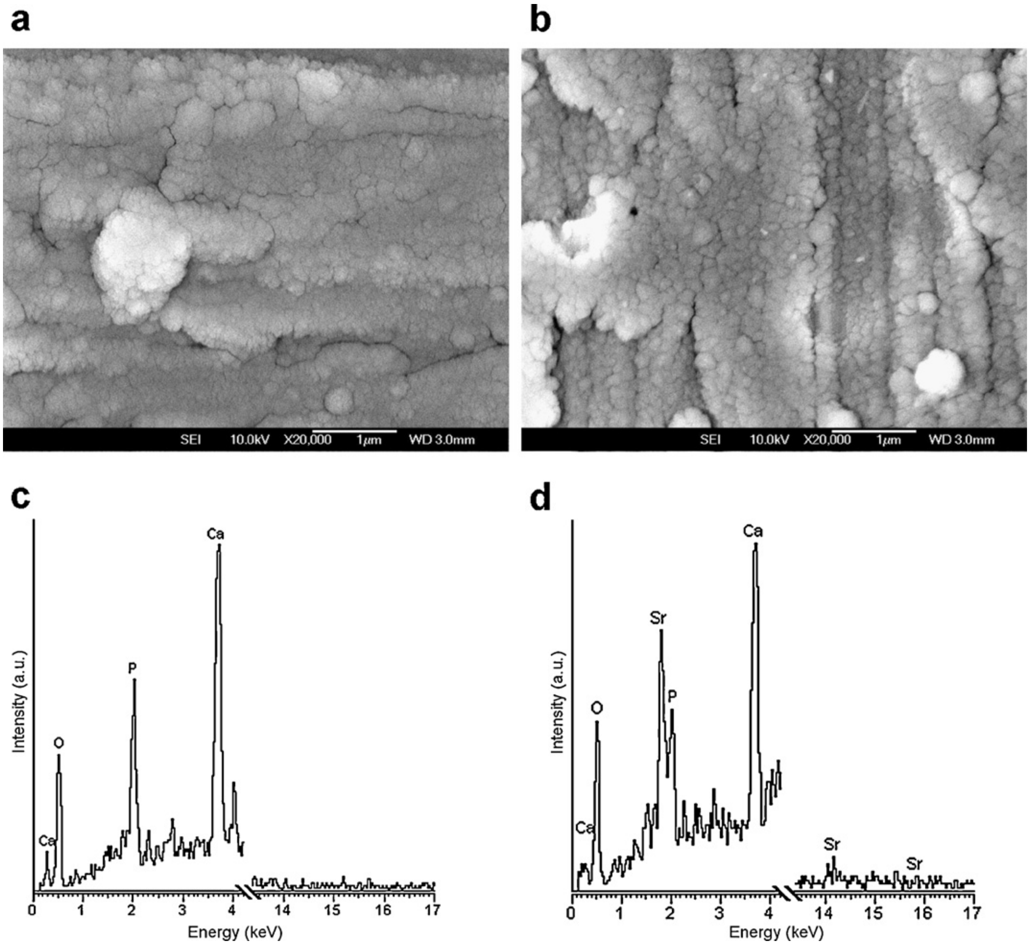

Fig. 1. SEM micrographs of the reference HA coating (RHA) (a), the coating produced from an ablation target of 10% Sr (RSr10.0) (b), EDS spectrum of RHA sample (c) and EDS spectrum of RSr10.0 sample (d).