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Spray-pyrolyzed hydroxyapatite thin-film coatings

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ABSTRACT

Hydroxyapatite (HA) thin-film coatings have been deposited on sheet substrates of a commonly used biomaterial (Ti6Al4V) using the spray pyrolysis technique. For this, a 0.042 M calcium spraying solution was prepared by dissolving calcium acetylacetonate hydrate in N,N-dimethylformamide, and phosphoric acid (H_3PO_4) was used as the source of phosphorous with different volume concentrations in deionized water. Both the solutions were supplied simultaneously and in parallel during the deposition of the coatings. The coatings were deposited at substrate temperatures of 425 and 525 °C. The use of 0.27% (volume) solution of H_3PO_4 resulted in coatings with stoichiometry close to that of the HA. The chemical composition, surface morphology and structure of the HA coatings were investigated by X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and X-ray diffraction (XRD). The characteristics of the coatings thus observed are presented and discussed. The high purity of the coatings was revealed by XPS, confirming the presence of Ca, P and O as the main constituents, with a Ca/P ratio of about 1.3. Some carbon, inherent to the precursors used, was also detected by XPS. The XRD patterns obtained suggested preferred (113) and (321) crystal orientations in the coatings.

1. Introduction

Hydroxyapatite ($Ca_5(PO_4)_3(OH)$, HA) is a bioceramic material that has been widely studied and used in the biomedical field due to its chemical composition, which is close to that found in human hard tissue. For this reason, HA presents properties such as excellent biocompatibility and osteoconductivity [1]. Plasma-sprayed HA coatings have been used on metallic bone implants for about 20 years now, but there are still many issues that continue to be addressed for improving the use of HA coatings for improved implant fixation. Plasma spray is a complex and expensive technique to set up and it is difficult to control the stoichiometry, phase composition and thickness of hydroxyapatite coatings [2]. Since the thickness of continuous plasma-sprayed HA coatings is generally in excess of 50 µm and the coatings are non-uniform and non-conformal, improvements to these coatings are desirable for imparting bioactivity to biomedical implants with finer dimensions such as screws for dental, craniofacial, external fixation and spinal fusion applications. In particular, the peak of the screw thread hardly gets coated due to heavy deflection of the depositing HA particles and the valley (base) of the screw thread gets filled up excessively, thus compromising the biomechanical aspects of such fine screws. In view of the above issues with plasma-sprayed HA coatings, deposition of thin (a few µm in thickness) HA coatings with high purity and crystallinity is being pursued, primarily aimed at realizing cost-effective coatings with improved adhesion and predictable properties. A range of deposition methods such as sputtering [3], pulsed laser deposition [4], electrodeposition [5–8] and growth from simulated body fluid [9] has been employed to achieve this goal with some success. However, the methods of sputtering and pulsed laser deposition are relatively complex and expensive, and hence new deposition methods are being investigated for HA coatings. One such method is ultrasonic spray pyrolysis (USP).

The work presented in this paper is motivated by the need to deposit cost-effective HA thin-film coatings with high purity and crystallinity. For this, we have employed the USP technique, a simple thin-film deposition method with low setting-up costs and capable of batch processing at atmospheric pressure in air at ambient conditions. The USP set-up we have used consists of an ultrasonic generator used for mist production from a spraying solution containing the precursor materials. The mist is transported to the substrate surface, which is heated to achieve the pyrolysis of the chemical solution, leading to a solid coating on top of the substrate [10,11]. USP-based methods have recently been used to deposit HA coatings [12,13]. For example, HA coatings were deposited on 316L stainless steel at a substrate temperature of 300 °C from calcium nitrate, ammonium dihydrogen phosphate and nitric acid [12]. In the work presented in this paper, the synthesis of HA coatings was achieved by using calcium acetylacetonate [Ca(acac), $C_{10}H_{14}CaO_4$], as the source of calcium, and H_3PO_4 as the source of phosphorus. In the work reported by Ye and Troczynsky [12], the as-deposited coatings were also subjected to an additional heat treatment at 600 °C in air for 5 h. In contrast, one of the main

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