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Feature article

Dense nanostructured calcium phosphate coating on titanium by cold spray

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ABSTRACT

This article deals with the understanding of building-up mechanisms of bioactive nanocrystalline hydroxyapatite coatings by Cold Spray, revealing very promising results in contrast to more conventional techniques such as Plasma Spray. A full characterization of feedstock and coatings is provided. The agglomerated structure of the powder proved to be suitable to obtain successfully thick hydroxyapatite coatings. A crystallite size below ~20 nm in the powder and the as-sprayed coatings is calculated by the Rietveld X-ray refinement method and agreed by Transmission Electron Microscopy. Some wipe tests were carried out on Ti6Al4V substrates in order to study the deposition of single particles and the nanoscale features were evaluated. The resulting structure indicates that there is no delimitation of particle boundaries and the overall coating has been formed by effective compaction of the original nanocrystallites, leading to consistent and consolidated layers.

1. Introduction

Hydroxyapatite plasma sprayed (PS) coatings have been widely used in orthopedic surgery to reconstruct hip and knee joints. Studies reveal that once HA is implanted, it has the ability to bond directly to the bone, to achieve earlier and greater fixation and to reduce the healing time. Moreover, these coatings can successfully reduce the incidence of thigh pain and femoral osteolysis [1]. Despite the existence of controversy between the use of hydroxyapatite (HA) coatings and porous metallic coatings, HA coatings have shown to have faster bone growth [2].

From all methods to produce HA coatings: dip coating, electrophoretic deposition, hot isostatic pressing, ion-beam sputtering, among others, PS appears to be the most favorable mainly because of the high deposition rates at low cost. Nevertheless, the high temperatures and high cooling rates from the PS technique lead to HA decomposition with the formation of a large content of amorphous phases. The ideal HA coating for orthopedic implants would be one with strong cohesive strength, good adhesion to the substrate and low porosity [3], while few works attempt to report a preferred value of crystallinity. Actually, much interest has arisen on nanocrystalline coatings due to the small crystal size which improves cell proliferation and, therefore, the osteoconductive properties of the coatings coming from their higher degradability [4]. Mainly due to the possibility of controlling coating crystallinity, low temperature depositing processes such as biomimetic deposition, electrochemical deposition and solution deposition, are of interest. However, some are time-consuming and their mechanical properties are poor. Others such as Cold Spray (CS) [5], Aerosol Deposition (AD) [6–8] and nano-particle deposition system (NPDS) [9,10] have become of interest during the last decade.

HA layers have already been successfully achieved by AD [11–13]. AD mainly consists on a carrier gas supply system with mass flow control, a powder chamber containing feedstock powder, and a deposition chamber with motored X–Y stage and a nozzle evacuated by a rotary vacuum pump; in addition, high vacuum conditions are necessary. Dense structures occur by the reduction of crystallite size by fracture or plastic deformation; however, the bonding mechanism between the fine particles themselves has not been clarified yet [8]. Dense nanostructured HA coatings on titanium were achieved by fracturing HA particles into nanoscale fragments to form highly dense coatings with a theoretical density of 98.5%. TEM micrographs reveal an average grain size of 16.2 nm and amorphous phases, nonetheless with a good bond-

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ing strength of 30.5 ± 1.2 MPa [11]. Further, a heat treatment at 400 °C was required to avoid amorphous HA phases, leading to an increase in average grain size up to 29.3 nm; heat treatments up to 500 °C further lead to a grain size of 99 nm, showing a decrease in biological properties. It was concluded that grain size significantly affects biocompatibility. Webster et al. [14] reported that osteoblast functions on ceramics with grains smaller than 100 nm were significantly enhanced compared with larger grains. So, the production of nanocrystalline HA coatings on titanium seems desirable for implants if it can be accomplished at low temperature.

A difference between AD and CS is that AD uses submicrometer particles as feedstock while CS was originally more suitable for metallic feedstock within the 5–50 μm sized range and does not use vacuum conditions. CS is a solid-state coating deposition method where feedstock powders are propelled toward a gas jet at supersonic velocities up to 1100 m/s and lower temperatures than the melting point of the material, with minimum thermal input. Metallic particles undergo plastic deformation and adhere to the substrate. Temperature- and oxygen-sensitive materials such as polymer and titanium are successfully densely deposited [15–17]. Due to the inherent brittleness, ceramic deposition by CS is still a challenge and ceramic particles are deposited as cermets [18] or co-deposited with other ductile materials (e.g titanium) [19,20].

Lately, the research of HA CS coatings has been carried out with a lot of interest within the biomedical field. Some attempts of spraying HA were performed on ductile substrate materials with successful results. Lee et al. [21] deposited a HA coating homogeneously onto polyetheretherketone (PEEK) disk implants enhancing in vitro biocompatibility and promoting in vivo osseointegration. Noorakma et al. [22] improved the biodegradability of magnesium alloy by the re-precipitation of an apatite layer as a consequence of HA coating onto a magnesium alloy and HA-graphene composites were deposited as well [23]. Recently, we focused on the deposition mechanisms of HA by CS and reported the feasibility of the deposition of sintered HA powders by dynamic fragmentation due to pore collapse + cracking and crushing mechanisms of the HA particles, with a considerable decrease in crystal size [24]. Apart from this, only numerical investigations have faced the issue of HA deposition by CS, primarily analyzing the influence of nozzle and particle geometry in particle velocity [25,26].

The present article is aimed at studying the build-up of CS coatings from an agglomerated nano-crystalline HA powder, and compare it with the previous studies for a porous sintered crystalline HA powder [24].

2. Materials and methods

An agglomerated powder from Medicoat (France) was used as feedstock. The particle size has been measured using a Laser Diffraction Particle Size Analyser Beckman Coulter LS 13320. The density of the powder was measured through the standard specification ASTM B-962-08; the density is evaluated introducing in a flask of 25 ml a known mass of the powder in consideration and filling with a high wettable liquid with a known density, here cyclohexanone. Knowing the density of the dissolvent, the powder density can be calculated the following Eq. (1) the real density:

$$\rho = \frac{m_p}{\left(25 - \frac{m_t - m_p}{\rho_{liq}}\right)} \quad (1)$$

where m_p is the mass powder introduced, m_t is the total mass (powder + cyclohexanone) and ρ_{liq} is the cyclohexanone density at working temperature. Thermogravimetry (TG) was carried out by SDT 2960 (TA instruments) while FTIR by Thermo SCIENTIFIC NICOLET In10 MX of reflection with MCT detector. FTIR measurements were carried out in a Scientific Nicolet iZ10 MX, using Attenuated Total Reflection (ATR) diamond corrector and a DTG detector in a reflectance mode from 4000 to 675 cm^{-1} with a resolution of 4 cm^{-1}. All Fourier transform infrared spectroscopy FTIR analysis were carried out in combination with ATR, providing excellent quality data and the best possible reproducibility. This is a sampling method that enables direct examination of samples without further preparation of liquids, gases or solids.

The morphological characterization of feedstock powder and HA coatings was performed by Scanning Electron Microscopy SEM (ProX Phenom) equipped with Energy Dispersive Spectroscopy (EDS) for microanalysis. The phase identification of the powder and coating were analyzed by a X'Pert PRO MPD diffractometer (PANalytical). A Rietveld analysis, using the FullProf software [27], was carried out to refine the lattice parameters, determine the crystallite size and to find the percentage of the crystalline and amorphous phase [28]. The Thomson-Cox-Hastings pseudo-Voigt profile function was used for the refinement and the instrumental resolution was also introduced. In order to achieve a good correlation between the calculated and the experimental diffractograms, the minimum value of the usual fit indicators of the FullProf software were monitored (i.e. the refinement should give a reduced chi-squared nearly equal to 1). The increase of peak half width respect the instrumental contribution is assumed to mainly come from the grain size and strain effects; the different proper parameters were fitted throughout the refinement. At each step, iteration cycles were conducted until convergence was reached. In order to evaluate the amorphous phase content, HA coating was detached from the substrate and crushed and mixed with a known weight of crystalline phase pattern, in our case alumina. It is possible to calculate directly the weight fractions of the crystalline phases W_J and the weight fraction W_{AM} of the amorphous phases just knowing the fraction in weight W_P of the pattern (experimental weighted alumina fraction) and the weight fractions of the phases, W_J^O, quantified from the Rietveld refinement (including that of the pattern W_P^O), with the following equations [28]:

$$W_J = \frac{W_J^0 - W_P}{W_P^0(1 - Wp)} \quad (2)$$

$$W_{AM} = \frac{W_P^0 - W_P}{W_P^0(1 - W_P)} \quad (3)$$

The Cold Gas Spray equipment used is a CGS KINETICS® 4000 (Cold Gas Technology, Ampfing, Germany) with a maximum operating pressure of 40 bar, temperature of 800 °C and operated with nitrogen as the propellant gas.

For the evaluation of single particle deposition, the so-called "wipe test" was performed, which consisted in particle deposition onto a mirror-like polished Ti6Al4V alloy substrate at high gun traverse speed.

The HA coated sample from previous studies [29] was used for the study of particle-particle interaction. In order to examine those features, a thin lamella from HA particle, single splat and coating were obtained by Focused Ion Beam (FIB) lift-out technique and compared to the initial feedstock structure. A FEI Strata Dual Beam 235 system was used. Finally, transmission electron microscopy examinations were carried out using a JEM 2100 microscope, operated at 200 kV (with current density of 80–250pA/cm^2). Much care was taken when irradiating the samples since some damage could be noticed through the observation; however, the use of a spread beam to acquire HRTEM images produces a decrease of the electron dose on the sample, which gave us the possibility to obtain such information without being significantly degraded.

In order to evaluate the adhesion, a Revetest (CSM Instrument) scratch equipment with a Rockwell C diamond indenter with a cone

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