Available online at www.sciencedirect.com
SCIENCE DIRECT®
Thin Solid Films 503 (2006) 69–78
thin solid films
www.elsevier.com/locate/tsf

Morphology of calcium phosphate coatings for biomedical applications deposited using Electrostatic Spray Deposition

S.C.G. Leeuwenburgh [a], M.C. Heine [b], J.G.C. Wolke [a], S.E. Pratsinis [b], J. Schoonman [c], J.A. Jansen [a,*]

[a] Department of Biomaterials, Radboud University Nijmegen Medical Center, Nijmegen, The Netherlands
[b] Particle Technology Laboratory, Department of Mechanical and Process Engineering, ETH Zürich, Switzerland
[c] Laboratory for Inorganic Chemistry, Delft University of Technology, Delft, The Netherlands

Received 31 August 2005; received in revised form 25 November 2005; accepted 25 November 2005
Available online 8 February 2006

Abstract

Electrostatic Spray Deposition (ESD) of biomedical calcium phosphate (CaP) coatings was investigated by in situ measurements of droplet sizes and velocities using Phase Doppler Anemometry. Processing parameters, related to the ESD-apparatus as well as the composition of the precursor solutions, were varied (deposition temperature, nozzle-to-substrate distance, nozzle geometry, and composition of the precursor solution). Thereafter, morphological characteristics of these ESD-derived CaP coatings were correlated with measured droplet characteristics. By varying physical apparatus-related parameters such as the nozzle-to-substrate distance and the deposition temperature, it was observed that electrosprayed butyl carbitol droplets did not shrink during droplet flight towards the heated substrate. Nevertheless, coatings with a different surface morphology were obtained, varying from microporous structures with coalesced pore walls to isolated rings on top of dense or grainy underlayers. The chemical composition of the precursor solutions and the mixing characteristics of the calcium and phosphate precursor components strongly influenced the initial droplet sizes, precipitation kinetics of the CaP solute, and subsequent coating morphology. Unique, reticular coatings can be deposited at a deposition rate of 3.2 μm/h, which have a graded structure consisting of a dense underlayer, a submicron-porous intermediate layer, and a roughened toplayer revealing droplet-derived features such as isolated rings or coalesced, hollow surface pits.

Keywords: Biomaterials; Coatings; Deposition process; Surface morphology

1. Introduction

Calcium phosphate (CaP) coatings are applied onto the surface of metallic implants, since these so-called bioactive ceramics are able to establish a tight, chemical bond between the implant surface and surrounding osseous tissue. This bone-bonding capacity is strongly related to the chemical properties of the coating surface upon exposure to body fluids [1–3]. In addition, the topography of biomaterial surfaces (in terms of physical factors such as surface roughness and porosity) is suggested to have a strong influence on biological processes such as the adsorption of proteins, cell adhesion and spreading, and consequently the overall tissue response in vivo [4]. In order to investigate this fundamental relationship between the chemical and physical nature of CaP coatings and their biological performance in vitro and in vivo, a flexible deposition technique is required which offers the possibility of varying both kinds of coating characteristics over a wide range. In that respect, the versatility of the Electrostatic Spray Deposition (ESD) technique regarding deposition of coatings with controlled surface morphology is particularly interesting. Briefly, the basic principle of ESD is the generation of a spray of charged, micron-sized droplets. This is accomplished by means of electrostatic atomization of precursor solutions. These spray droplets are directed towards a grounded and

* Corresponding author. Radboud University Nijmegen Medical Center, Department of Biomaterials, P.O. Box 9101, 6500 HB Nijmegen, The Netherlands. Tel.: +31 24 3614006; fax: +31 24 3614657.
E-mail address: j.jansen@dent.umcn.nl (J.A. Jansen).

0040-6090/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2005.11.116

heated substrate as a result of the applied potential difference. After complete solvent evaporation, a thin layer is left onto the substrate surface.

Several studies have shown already that inorganic [5–7], polymeric [8], as well as protein coatings [9] can be deposited using ESD with a wide variety of surface structures. Specifically, the ESD technique was shown to enable synthesis of biomedical CaP coatings with defined chemical [10] and morphological [11] characteristics. Under certain conditions, a unique reticular coating morphology was obtained, characterized by a three-dimensional, interconnected pore network with variable pore size. From a biomedical point of view, this coating morphology offers the advantage of creating an implant surface with an increased and controllable surface area. As a result, phenomena such as CaP coating dissolution rate and incorporation of osteoinductive proteins might be controlled by tailoring the surface morphology.

Various formation mechanisms have been suggested in the literature to explain the characteristic surface morphologies obtained using ESD. However, these models are merely based on observations using Scanning Electron Microscopy (SEM), and in some cases the models are contradictory. For example, Chen et al. [5] reported that it is necessary to use a solvent with a high boiling point (for example butyl carbitol, T_b=231 °C) in order to deposit dense $LiCoO_2$ coatings, whereas Perednis et al. [7] observed the opposite effect by depositing dense yttria-stabilized zirconia (YSZ) films using a solvent with a low boiling point (1-methoxy-2-propanol, T_b=120 °C). Based on a theoretical model for evaporation of electrospray droplets during transport towards a hot plate [12], Wilhelm et al. developed a deposition diagram describing the surface texture of ESD-derived YSZ coatings as a function of initial droplet size, precursor concentration and substrate temperature. This model was in agreement with experimental results obtained using a Phase Doppler Anemometer (PDA), which enables characterization of electrospray droplet sizes and velocities [13].

Here, a PDA was used to characterize the electrosprays in situ during formation of CaP coatings at high deposition temperatures. Morphological features of ESD-derived coatings were correlated with the corresponding droplet characteristics of the electrosprays. The influence of several physical (apparatus-related) and chemical (solution-related) deposition parameters (deposition temperature, nozzle-to-substrate distance, nozzle geometry, and the composition of the precursor solutions) on electrospray characteristics and coating morphology was investigated. The physical, apparatus-related parameters (deposition temperature and nozzle-to-substrate distance) were chosen for their supposed influence on solvent evaporation, whereas the geometry of the spraying nozzle was supposed to affect the mixing characteristics of the precursor solutions. The influence of the chemical composition of the precursor solutions was investigated, since it is known that physical properties of the precursor solutions (such as electrical conductivity) strongly determine the initial droplet properties in the process of electrospraying [14,15].

2. Experimental details

2.1. Electrostatic Spray Deposition set-up

In the current study, the spray was directed from the nozzle downwards to the heated substrate. A direct current voltage supply (Bertan 450, USA) was used in order to generate a positive high potential difference between the nozzle and grounded substrate, which was heated by a heating plate (Ceran 500, Type 11A, Germany). Two precursor solutions containing either Ca or P precursor salts were pumped simultaneously towards the spraying nozzle with a single syringe pump (Bioblock Scientific, A99, France). Ca and P precursor solutions were prepared by dissolving $Ca(NO_3)_2{\cdot}4H_2O$ (Merck) and H_3PO_4 (85 wt.%, J.T. Baker) in butyl carbitol ($C_8H_{18}O_3$, 99%, Aldrich). A stable cone-jet mode of electrospraying was generated by adjusting the potential difference between the spraying nozzle and substrate between 5.5 and 8.0 kV, depending on the specific set of deposition parameters. Characteristics of this cone-jet mode of electrospraying were described elsewhere [14–16]. Machined, commercially pure titanium (Ti) discs (diameter 12 mm, thickness 1.5 mm) and smooth silicon (Si) wafers (thickness 0.5 mm, WaferNet GmbH, Germany) were used as substrate material for the deposition of the CaP coatings. The substrates were cleaned ultrasonically in acetone (15 min) and ethanol (15 min) prior to deposition.

2.2. Coating deposition parameters

Deposition temperatures ranged between 25 and 400 °C, whereas the distance between the spraying nozzle and the substrate was varied between 20 and 40 mm. Regarding the geometry of the spraying nozzle, a two-component nozzle (Fig. 1, left) with separate inlet for Ca and P precursor solutions was used as standard nozzle (stainless steel, flat outlet, inner and outer diameter of 0.9 and 1.4 mm, respectively) in order to avoid premature precipitation of the precursor solutions within the nozzle prior to spray generation. This two-component nozzle geometry was compared with a conventional one-component nozzle geometry (Fig. 1, right) with equal

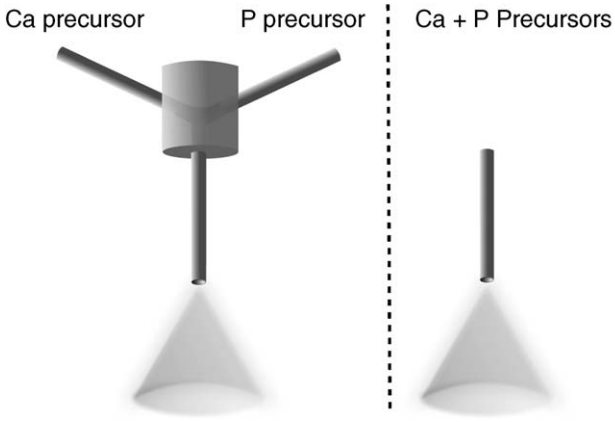

Fig. 1. Novel two-component (left) and conventional one-component (right) spraying nozzle geometries for ESD.