Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 40 (2014) 6949–6955

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Biomimetic deposition of hydroxyapatite on the surface of silica thin film covered steel tape

Božana Čolović[a], Vukoman Jokanović[a,*], Bojan Jokanović[b], Nataša Jović[a]

[a]*Institute of Nuclear Sciences "Vinča", University of Belgrade, Mike Petrovića Alasa 12-14, 11351 Belgrade, Republic of Serbia*
[b]*SGL Carbon, Meitingen, Germany*

Received 18 November 2013; received in revised form 3 December 2013; accepted 4 December 2013
Available online 14 December 2013

Abstract

The biomimetic deposition of hydroxyapatite (HA) on the surface of SiO_2 thin film coated metal substrates was developed and investigated.

The structural investigations of HA were made by XRD and FTIR-ATR, while morphological and chemical changes during HA biomimetic deposition on the surfaces of silica thin films were investigated by SEM with EDS.

The HA film thicknesses were estimated from the mass changes of samples including the corresponding correction of the pore volume inside of them, which was calculated by the Lecloux and Pirard method based on the Dollimore–Heal method.

Keywords: A. Films; B. XRD methods; D. Apatite; SiO_2

1. Introduction

Recently, calcium hydroxyapatite (HA; $Ca_{10}(PO_4)_6(OH)_2$), the main inorganic constituent of bones and teeth, has been intensively studied as a potential material for the production of advanced bone grafts and implants. It can be used as a powder for dental fillings or as sintered blocks for modeling/remodeling of bone defects, replacing allografts, as well as coatings of metallic implants etc. [1–4].

One of the most important applications of various oxides and HA is their use in the form of thin films, deposited on the surfaces of metal substrates (mostly made of titanium alloys), which are preferentially produced by plasma spraying method. These thin films/coatings have been found to improve the adhesion of structural prostheses and to reduce particle release from metal substrates. However, lack of bonding strength of these coatings to the metallic bio-inert substrate has been observed in in vivo tests. Failure in the form of general resorption of these coatings has also been described [5–8].

The presence of other calcium phosphate phases of lower stability, intrinsically related to the deposition technique, was indicated as the responsible factor. This disadvantage, mainly found in HA films deposited by plasma spraying, led to the use of alternative techniques for HA deposition (r.f. sputtering [9], r.f. magnetron spattering [10,11], pulsed laser deposition [12], laser ablation [13], sol–gel processes [14] and diverse electrochemical methods [15]). In order to find a new, more suitable deposition technique, the mechanism of HA nucleation and growth in a simulated body fluid (SBF) was also studied. In these systems, the deposition was initiated by Ca nucleation on the substrate, which triggered the HA formation [5,6].

Recent investigations of biomimetic processes have focused on the designing of bioactive coatings with HA layers deposited both onto inorganic and organic substrates, using SBF with ionic concentrations nearly equal to (or higher than) those in human extracellular fluid. Once the HA nuclei are formed on the substrate surface, even under normal conditions, since SBF is supersaturated with salts containing Ca^{2+} and PO_4^{3-} ions, they grow spontaneously to give a HA layer. Of course, the main objective of this engineering is to create the corresponding thin films as sub-layers, which can enable an effective induction of HA nucleation, as it occurs in the living

*Corresponding author. Tel.: +381 641748636; fax: +381 113408607.
E-mail address: vukoman@vinca.rs (V. Jokanović).

0272-8842/$ - see front matter © 2013 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2013.12.018

body during formation of bones and teeth. This process strongly depends on the activity of inorganic or organic sub-layers. In general, the main aspects of the activity of sub-layers at inorganic interfaces are the concentration of cations in SBF and the structural correspondence of HA layers and inorganic sub-layers with corresponding stereochemical requirements. In agreement with this, negatively charged surfaces, like the surface of bioactive silica, are always favorable for the heterogeneous HA nucleation in a supersaturated solution of SBF. Therefore, the accumulation of Ca^{2+} ions due to electrostatic attraction increases the supersaturation near the negatively charged surfaces, and as a result, the initial nucleation is preferentially triggered. The nucleation and growth of HA layers provide a better insight into bioactive behavior of silica-based materials. These highly reactive materials cause a local decrease of Ca^{2+} and PO_4^{3-} ions in the surrounding solution during HA formation, which can induce the acceleration of HA nucleation [16–20].

2. Experimental

2.1. Deposition of HA thin films

The SiO_2 covered steel tapes, obtained as described in Appendix A, were immersed in SBF at 37 °C, to allow biomimetic formation of HA thin film on its surface. SBF was prepared by a slightly modified recipe ($c_{Cl^-}=0.054$ mol/L; $c_{Na^+}=0.0542$ mol/L; $c_{Ca^{2+}}=0.0025$ mol/L; $c_{PO_4^{3-}}=0.001$ mol/L; $c_{Mg^{2+}}=0.0003$ mol/L; $c_{CO_3^{2-}}=0.0006$ mol/L and $c_{K^+}=0.0014$ mol/L), where PO_4^{3-} and Ca^{2+} concentrations were shifted slightly over the boundary of solubility of these ions in HA, given by their solubility product ($PS=2.34\times10^{-59}$) [21,22]. The immersion times of samples in SBF were 10, 20, 30 and 40 days, and SBF was refreshed every 48 h. After that, the samples were removed from the SBF, carefully rinsed with deionized water and prepared for subsequent SEM, EDS, BET, XRD and FTIR-ATR investigations.

2.2. Characterization methods

The morphology, size distribution and the average size of HA particles were determined by scanning electron microscopy, SEM, (JEOL: JKSM-5300). The samples were prepared by coating the powder with gold using the PVD method. The particle size was determined by applying the line intersection method on a scanning microphotograph with over 200 particles for each sample. An energy dispersive spectrometer (QX 2000 – Oxford Instruments) combined with SEM and a multichannel analyzer was used to estimate the chemical homogeneity of synthesized HA. The chemical homogeneity was assessed via Ca/P intensity ratio using the ZAF (Link Company) software package, which compares the intensity of the X-ray fluorescent emission from the surface of synthesized HA with that of the standard sample.

EDS (energy dispersive analysis) measurements were performed in order to detect chemical homogeneity of the obtained phase and ratio of Ca, Mg, Na and P.

The nitrogen gas absorption BET method (Sorptomatic 1990, Termoquest CE Instruments) was used for the determination of the specific surface areas of HA powders. The samples (0.20–0.22 g) for absorption measurement were thoroughly degassed at 150 °C for 3 h. Knowing the absorbed volume of N_2 (purity 99.99%), the specific surface areas of HA powders were determined applying the BET method (based on the correlation $p/(V_{ads}(p_o-p))$ vs. p/p_o, where p_o is the saturation pressure, p is the equilibrium pressure and V_{ads} is the absorbed volume of nitrogen). The Dubinin Radushkevich method (correlation $\log(V_{ads})$ vs. $\log_2(p_o/p)$ was used for the determination of the specific surface area, too. The average and the maximum radius of pores and the cumulative volume of all pores were determined using the Lecloux and Pirard method based on the Dollimore Heal pore-sizes standard absorption isotherm.

Structural analysis of biomimetically obtained HA was performed by the X-ray diffraction (XRD) method. For XRD analysis Philips PW 1050 diffractometer with Cu-K$\alpha_{1\text{-}2}$ lamp was used, and the data were collected in the 2θ range from 9° to 67°, in steps of 5° and an exposure time of 2 s per step.

The phase investigations were performed using FTIR-ATR spectroscopy (Nicollet 380 FT-IR, Thermo Electron Corporation) and XRD analysis (Philips PW 1050) with Cu-K$\alpha_{1\text{-}2}$ radiation.

3. Results and discussion

3.1. SEM investigations

Typical structure of HA nucleated on the surface of SiO_2 thin film, which includes shape, size distribution of basic HA particles and their agglomerates, was the main subject of SEM investigations (Fig. 1).

The light spots in Fig. 1a present the top of agglomerates, while the darker spots show places with thinner layers of HA, nucleated after 10 days. The morphology and density of the film was obviously different along the film surface, showing characteristic roughness. The smallest HA particles were 0.125–0.250 μm in size, while the sizes of agglomerates were 0.3–1.25 μm (Fig. 1a). Inside of them, closed rings, like chains, with diameters of 1.25–2.25 μm, with 0.6–0.75 μm voids between, were observed.

As it can be seen in Fig. 1b, for the HA nucleation time of 20 days, the size of the smallest particles was between 0.16 and 0.33 μm, while the sizes of agglomerates were 0.5–0.66 μm (the smallest and the most numerous), between 0.8 and 1.66 μm (medium), and up to 2.5 μm (the largest agglomerates). The agglomerates were interconnected in the form of chains, with voids in size range of 0.5–0.7 μm inside of them.

The HA layer after 30 days of nucleation (Fig. 1c) consists of small HA particles 0.067–0.166 μm in size, as well as small (0.4–0.83 μm) and large (1.66–3.86 μm) agglomerates. The large agglomerates are composed preferentially of small agglomerates, which formed a characteristic structure with many, in various ways, interconnected branches of HA.