CHARACTERIZATION OF HYDROXYAPATITE COATINGS OBTAINED ON DIFFERENT METAL SUPPORTS USING TWO ELECTRODEPOSITION METHODS

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Abstract

The naturally originating or synthesized calcium apatite inorganic mineral known as hydroxyapatite (HA), with the chemical formula $Ca_{10}(PO_4)_6(OH)_2$, is a very promising biomaterial for applications in the orthopedics and dentistry fields, such as bone repair and dental implants [1,2]. However, HA is also a brittle ceramic and because of this it has to be used in combination with metallic or polymeric reinforcing materials [3,4]. Implants obtained by coating HA (as such or doped) on metal substrates benefit from the properties of the ceramic layer that promotes osseointegration [5], prevents metal atom diffusion [4] and has an anticorrosive effect [6], as well as from those of the support that provides fracture, wear and corrosion resistance [3,7]. Various methods are being used for applying the HA coating onto metal substrates [8,9] and the method selection stage from the implant manufacturing process is especially important.

In a previously published paper [3] we described a novel HA electrochemical deposition method, in which one of the two precursors used to synthesize HA (either the phosphate precursor or the calcium one) was present in the electrolysis cell, while the other was added dropwise, simultaneously with the application of the electrochemical potential required to electrocoat the Ti substrate. The current work continues the previous one by comparatively analyzing the HA coatings obtained on different metal supports using the novel electrodeposition method, as well as the standard one [10].

The HA precursors selected for the study were $Ca(NO_3)_2 \times 4H_2O$ and $(NH_4)_2HPO_4$ (equal volumes of 1.75 mM and 1.05 mM solutions, respectively). The metal substrates were polished disks of Ti, Cu, Ni and C55 stainless steel. A potentiostat, a glass cell with heating mantle connected to a thermostat set at 80°C, a Pt plate anode, and a Teflon casing containing each metal disk were used to obtain the HA coated samples. The duration of each experiment was 4 hours, at an applied potential of −1.5 V. Two specimens were obtained for each type of metal substrate - one by using the standard electrodeposition method and the second by employing the novel method. When the novel method was utilized, the added precursor was the Ca precursor. Each of the eight samples was characterized via X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and atomic force microscopy (AFM).

Based on the recorded XRD patterns, for the HA coatings on Cu, Ni, and stainless steel substrates obtained using the standard method only small amounts of electrodeposited crystalline HA were observed. However, larger amounts were formed with the novel method, which indicates that this approach is a more effective way of growing HA crystals on the aforementioned supports. In the case of the Ti substrate, the HA crystallinity was slightly improved when the standard deposition method was employed, but for the sample obtained with the novel method a preferential growth along the c-direction was identified that was more intense than for the specimen resulted using the standard method.

The SEM images recorded on the HA coatings electrodeposited with the novel method revealed a higher degree of uniformity and continuity compared with the coatings applied by

utilizing the standard electrochemical deposition approach. This observation concerns all the types of metal substrates considered in the study.

The conclusions reached based on the SEM data were backed up by the observations made during the AFM characterization of the samples. The 2D and 3D AFM micrographs recorded on the specimens revealed the differences between the coatings obtained using the two deposition methods. In the case of the novel method, the coatings displayed a higher degree of uniformity and continuity than the ones resulted by employing the standard method. A deeper understanding of the differences was made possible by considering the AFM data to calculate the values of several AFM parameters. For example, from among all the specimens, the one obtained on Cu support with the standard deposition method was found to have the highest surface roughness.

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