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The nanostructure of an electrochemically deposited hydroxyapatite coating

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ABSTRACT

The structure of an implant's coating can significantly affect its physical and chemical properties, and eventually – its clinical performance. In this paper, the nanostructure of an electrochemically deposited hydroxyapatite (EDHA) coating was studied by X-ray diffraction (XRD), scanning electron microscopy (SEM), and high-resolution transmission electron microscopy (HRTEM). The X-ray analysis showed that the coating consisted predominantly of the stoichiometric HA phase. However, SEM and HRTEM revealed that EDHA coating is composed of two distinct regions: the upper layer consisted of platelet crystallites preferentially grown perpendicular to the substrate surface, while the lower layer was dense and uniform and consisted of nano-sized crystallites of HA. The possible effects of these different microstructures on the implant's after-implantation behavior are discussed.

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1. Introduction

The last decade has seen the dramatic increase in the study of electrochemically deposited calcium phosphate coatings as potential substitutes for plasma-sprayed hydroxyapatite (PSHA) coatings in orthopaedic surgery [1–3]. Various calcium phosphate coatings, including carbonated apatite [4], brushite (dicalcium phosphate dehydrate, DCPD) [5], octacalcium phosphate (OCP) [6,7], and hydroxyapatite (HA) [8,9], have been successfully applied to titanium-base and other alloys by electrochemical deposition. Compared to plasma spraying, the advantages of electrochemical deposition include good control of composition and structure of the coating, the relatively low processing temperature, the ability to deposit on porous or complex shapes, lower cost, etc. [1]. The structure of the deposited coatings can be controlled by changing the composition, pH and temperature of the electrolyte, as well as the applied potential or current density [10].

In vivo study [11] has demonstrated that electrochemically deposited hydroxyapatite (EDHA) has similar osteointegration compared to PSHA after implantation in a canine model. A following *in vivo* study in rabbits [12] approved that electrochemical deposition of HA following NaOH soaking can further improve the bone apposition ratio and the new bone area around titanium alloy implants. A related *in vitro* study [13] also showed that electrodeposition of HA provided the highest surface area and induced the highest osteoblast cell attachment. By real-time electrochemical atomic force microscopy (ECAFM) and X-ray photoelectron spectroscopy (XPS) analysis, Eliaz and his colleagues studied the coating formation mechanisms and suggested

there were two stages in the electrodeposition of HA: a stage of instantaneous nucleation and two-dimensional growth, followed by a stage of progressive nucleation and three-dimensional growth; a layer of OCP formed first as the precursor phase, while the HA most likely formed subsequently via transformation, rather than directly [14].

It is widely believed that a coating's *in vivo* behavior can be greatly affected by its structure (phase content, texture, crystal size, surface morphology, size and distribution of pores, etc.) [15]. Despite the progress in EDHA studies, the understanding of its nanostructure is still very limited due to the difficulties in sample processing. Thus, an in-depth study of the structure of the EDHA may shed more light on its unique characteristics that are responsible for its good biological performance as evident in the early studies, and may result in further modifications in the coating deposition procedures in order to obtain coatings with even higher quality and better clinical performance. In this letter, we report that the first direct observation of these two layers by scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM).

2. Materials and methods

A Ti-6Al-4V ELI grade rod (Titanium Industries), 4.76 mm in diameter, was machined into 10.0 mm-long sample rods. Thirty rods were electrochemically deposited as in [11]. In brief, electrodeposition was carried out in a standard three-electrode cell containing 0.61 mM $\text{Ca}(\text{NO}_3)_2$ and 0.36 mM $\text{NH}_4\text{H}_2\text{PO}_4$ (Merck, Darmstadt, Germany) at 85 °C. An EG&G/PAR (Princeton, NJ) model 263A potentiostat/galvanostat operating in potentiostatic mode was employed to maintain the cathode potential at -1.4 V vs. SCE for 2 h.

The near-surface phase composition was studied by powder X-ray diffractometry (RU300, Rigaku). The surface morphologies were imaged by ESEM (Philips model XL30, FEI/Philips). Then, samples were embedded in Spurr's resin (Ted Pella), cut into 0.5 μm -thick

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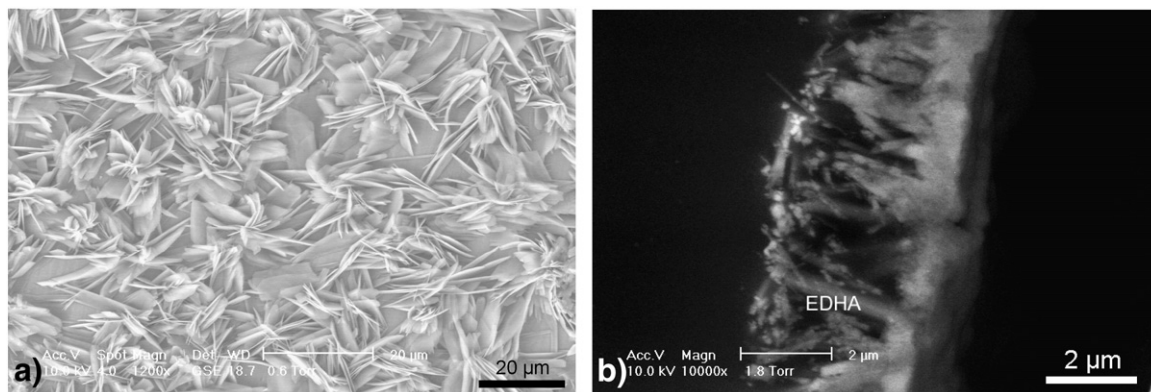


Fig. 1. ESEM images of the EDHA coating: (a) surface top view, (b) cross-section.

slices, ground and polished. The polished specimens were subsequently coated with carbon, and the cross-sections were observed by ESEM. To prepare TEM samples, slices were freeze-fractured to remove the titanium alloy and then observed under a light microscope to ensure that the coating/resin interface was maintained intact. After removing the titanium, the samples were re-embedded in Spurr's resin. Thin sections, about 60–80 nm thick, were cut by an ultramicrotome (Boeckeler Instruments), collected on parlodion-coated grids (Ted Pella), and air-dried. The microtomed samples were viewed under JEM 2010 F TEM instrument (JEOL Inc., Tokyo, Japan). Elemental analysis was made using an energy-dispersive X-ray spectroscopy (EDS) detector attached to the TEM instrument.

3. Results

XRD confirmed that the EDHA coating consisted mainly of the stoichiometric HA phase. SEM image from the top view showed clusters of plate-like crystals nearly perpendicular to the substrate (Fig. 1a). The side-view showed that the thickness of the EDHA coating was about 5 μm , and clearly revealed two distinct layers: (1) a uniform, 500-nm thick dense layer adjacent to the substrate, and (2) a thicker but looser top layer composed of crystals with varying sizes, vertical to the substrate surface (Fig. 1b).

High-resolution TEM images revealed the atoms arrangement in the two layers within the EDHA coating. A dense layer, composed of crystals with size of about 50 nm or less, was found at the bottom of the coating (circles in Fig. 2a). Apparently, a rapid nucleation of HA occurred at the very beginning of the electrochemical deposition process, and many tiny HA crystals formed in this way; but, only HA

crystals in favorable orientations could further grow, thus forming large single crystals (Fig. 2b). A selected area electron diffraction pattern from the bottom layer showed poly-crystal diffraction rings (inset in Fig. 2a), while diffraction from the crystals in the upper layer showed single crystal character (inset in Fig. 2b). A fringe pattern with 8.2 \AA repeat period, representing the (100) planes of the hydroxyapatite lattice, was observed. Elemental analysis by EDS confirmed that both layers were mainly composed of Ca, P, and O, and established that for both layers the Ca/P atom ratio was close to that for HA (upper layer: 1.60, bottom layer: 1.67, stoichiometric HA: 1.67).

4. Discussion and conclusions

Two distinct layers were observed in the EDHA coating. The whole coating deposition process was a reminiscent of dendritic growth, which is in agreement with a previous AFM study [3]. These findings support the occurrence of both instantaneous and progressive nucleation mechanisms, as well as the transition from two-dimensional to three-dimensional growth first suggested by Eliaz and Eliyahu [3]. However, no OCP has been observed in the bottom layer. It could either already transfer into HA or its amount is too little to be distinguished by selected area diffraction and elemental analysis.

This study also showed that the EDHA obtained in this experiment is highly crystalline. The lower solubility of the highly crystalline coating could remain as a concern. If an outer thin layer of coating could be engineered to be amorphous or nanocrystalline HA, the solubility *in vivo* would doubtless increase in the short-term, thus accelerating the kinetics of initial bone formation. The underlying crystalline HA could still aid in extending the lifetime of the coating *in*

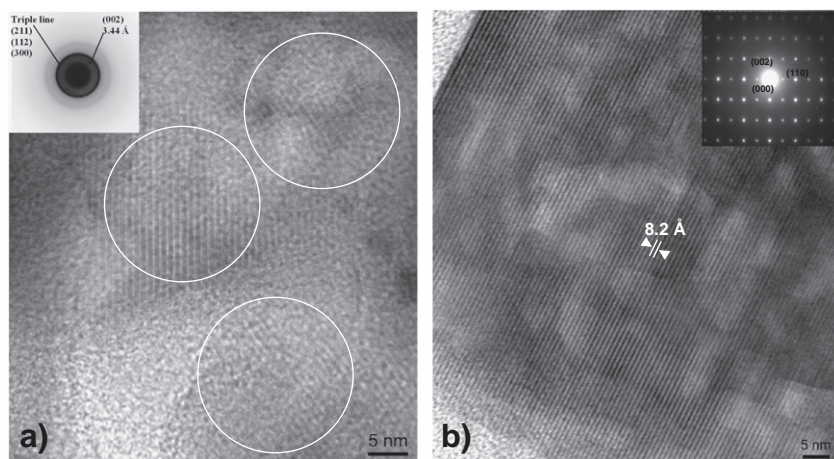


Fig. 2. High-resolution TEM for (a) bottom layer, and (b) upper layer of EDHA coating.

vivo. Such a functionally graded coating could possibly be realized during electrodeposition by changing the applied potential or applying pulsed deposition. It has been shown [16] that even much thinner HA coatings could prove efficacious over the critical weeks to months of periods for establishment of apposing mineral tissue before substantial remodeling occurs.

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