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Deposition and investigation of functionally graded calcium phosphate coatings on titanium

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Abstract

A series of calcium phosphate coatings with graded crystallinity were deposited onto heated titanium substrates using ion beam assisted deposition. The microstructure of the coating was examined using transmission electron microscopy (TEM). The coating thickness was observed to be in a range of 594–694 nm. The degree of crystallinity and microstructural grain size of the coating showed a clear decrease with increasing distance from the substrate–coating interface. Fourier transform infrared spectroscopy (FTIR) confirmed the presence of PO_4^{3-}, and X-ray photoelectron spectroscopy (XPS) analysis on the coating top surface showed that the atomic Ca/P ratio was in the range of 1.52 ± 0.15 to 1.61 ± 0.07. The biological response to the coatings was also evaluated using an osteoblast precursor cell culture test. More cells and a higher integrin expression of cell attachment sites were observed on the coating surface when compared to the control group (blank titanium surface). The pull-off test showed average adhesion strengths at the coating–substrate interface to be higher than 85.12 ± 5.37 MPa. Nanoindentation tests indicated that the Young's moduli of all coatings are higher than 91.747 ± 3.641 GPa and microhardness values are higher than 5.275 ± 0.315 GPa. While the adhesion strength results helped us to identify the best setup for substrate temperature and processing parameters to begin the deposition, the culture test and XPS results helped identifying the optimum parameters for the last stage of deposition. TEM, X-ray diffraction, FTIR and nanoidentation results were used to further evaluate the quality of the coating and optimization of its processing parameters.

Keywords: Calcium phosphate coatings; Biomedical implants; Bioactivity; Adhesion strength

1. Introduction

Hydroxyapaptite (HA, $Ca_{10}(PO4)_6(OH)_2$), an inorganic mineral which makes up 70% of biological bone [1], has been widely used as an artificial bone material for coating biomedical implants. It has been shown that HA-coated biomedical implants are able to enhance bone ingrowth and osseointegration [1–5] due to their excellent biocompatibility and bioactivity [6–10] when compared to non-coated implants. The only commercial technique for producing HA coatings on metallic implants is plasma spraying, which utilizes a plasma flux of high temperature to spray partially melted HA powder onto the surface of implants [11–15]. However, problems associated with implants coated by plasma spraying—e.g. low adhesion strength of the coating to substrate (ranging between 3 and 15 MPa [12,15,16]), low mechanical stability of coating itself, nonuniform microstructure and crystallinity of the coatings—limit the performance and lifetime of implants. More advanced coating methods, such as ion beam sputtering deposition (IBSD) and ion beam dynamic mixing deposition (IBDM) have been studied to deposit HA coatings with higher adhesion strengths. The bond strengths of these coatings are enhanced by atomic bonding at the interface, densification of the coating and lower thermal stresses compared to plasma-sprayed coatings.

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The adhesion strength of these coatings are reported to be in the range of 8.02–45.82 MPa for IBSD [17] and 41.7–59.0 MPa for IBDM [18] coated samples. However, the as-deposited coatings are amorphous in all cases and post-deposition heat-treatment is necessary to crystallize the coating and improve its chemical stability in the body. It was reported that the degree of crystallinity of calcium phosphate coatings is influenced by heat-treatment temperature, time and the presence of water vapor [19–21].

In this study, calcium phosphate coatings with graded crystallinity were deposited on titanium substrates using ion beam assisted deposition (IBAD) in order to optimize the bioactivity, chemical stability and mechanical properties of the coating. The crystalline gradient was introduced by manipulating the substrate temperature during deposition. Several advantages over the traditional uniform coating are expected with functionally graded coatings processed by IBAD [22–26]. First, osseointegration is enhanced in early stages after implantation by the readily dissolved amorphous top layer, while the crystalline bottom layer is responsible for the stability and integrity of the coating. Second, the coating bonds to the substrate on an atomic level as a result of intermixing of coating and substrate atoms due to the effect of the ion beam, which leads to better and more consistent adhesion strengths than plasma-sprayed coatings [27]. Moreover, the thin calcium phosphate coatings (<1 μm thickness) provide a higher mechanical strength and better fracture resistance than thicker plasma-sprayed coatings. Finally, the in situ heat treatment allows the growth of films with varying crystal structures without the need for post-deposition annealing, resulting in shorter processing times and lower cost.

2. Materials and methods

2.1. Materials preparation

A series of calcium phosphate coatings were deposited onto titanium substrates using IBAD with varying substrate temperatures in order to fine-tune the processing parameters. Titanium discs of 7.62 mm thickness were machined from a 12.7 mm diameter, 99.5% commercially pure titanium rod (Alfa Asear). Prior to coating deposition, the substrates were prepared by wet grinding with 240, 400 and 600 grit silicon carbide paper (Buehler) and subsequent polishing with 9, 3 and 1 μm polycrystalline diamond suspension (Buehler). In between each of the grinding and polishing steps the discs were washed and ultrasonically cleaned to prevent cross-contamination of abrasive particles. After polishing and grinding, the discs were ultrasonically cleaned in acetone and isopropyl alcohol for 10 min each and passivated by exposing the discs to a 40 vol.% nitric acid solution at room temperature for 30 min. The discs were then rinsed with water and dried by compressed air (ASTM F86-91).

The calcium phosphate coating was processed using IBAD (Ion Tech) with a base pressure of 1.2×10^{-4} Pa using a 15.24 cm diameter HA target (Cerac Inc., 99% purity) recessed into a stainless steel holder. The coatings were deposited over 6 h with substrate temperatures from 650 to 400 °C in three scenarios A, B and C as shown in Table 1. For each of the depositions, 23 titanium disc substrates were secured into a custom-made stainless steel substrate holder. Substrate temperature was monitored with a thermocouple placed in the substrate holder and maintained within 5 °C of the targeted temperature over the duration of deposition. Prior to coating deposition, thermocouple readouts were verified by an optical pyrometer (Mikron M90). For the duration of the depositions, the beam voltage and current density for primary source were 1000 V and 2.0 mA cm^{-2}, respectively, whereas those of assist (secondary) source were 400 V and 0.5 mA cm^{-2}, respectively. In addition, 3 sccm of argon gas flow was provided to each ion source for the duration of runs.

2.2. Coating characterization

The morphology of the coating cross-sections was observed by transmission electron microscopy (TEM, Hitachi HF-2000). The samples for TEM analysis were prepared using the in situ lift-out technique associated with the FEI 200 focused ion beam (FIB) system.

The crystallinity of the coating was evaluated by X-ray diffraction (XRD, Xpert-Pro powder diffractometer). Coatings were analyzed with Cu Kα1 ($\lambda = 0.1540598$ nm) radiation, scanned between 20° and 80° for 2θ with a step size

Table 1
Summary of the thickness coatings A, B and C evaluated using TEM observation and their various layers as a function of deposition temperature.

Coating	Total thickness (nm)	Deposition temperature (°C)	Structure	Layer thickness (nm)
A	694	650	Columnar and crystalline	190
		550	Semicrystalline or amorphous without features	226
		450	Amorphous without features	278
B	594	600	Porous and crystalline	160
		500	Mostly amorphous with columnar crystals	200
		400	Amorphous without features	234
C	657	550	Columnar and crystalline	No obvious border among three layers
		500	Columnar and semicrystalline	
		450	Amorphous without features	