Correlation between surface properties and wettability of multi-scale structured biocompatible surfaces

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Abstract. The influence of surface properties of radio-frequency (RF) magnetron deposited hydroxyapatite (HA) and Si-containing HA coatings on wettability was studied. The composition and morphology of the coatings fabricated on titanium (Ti) were characterized using atomic force microscopy (AFM) and X-ray diffraction (XRD). The surface wettability was studied using contact angle analysis. Different geometric parameters of acid-etched (AE) and pulse electron beam (PEB)-treated Ti substrates and silicate content in the HA films resulted in the different morphology of the coatings at micro- and nano-scale. Water contact angles for the HA coated Ti samples were evaluated as a combined effect of micro-roughness of the substrate and nano-roughness of the HA films resulting in higher water contact angles compared with acid-etched (AE) or pulse electron beam (PEB) treated Ti substrates.

1. Introduction
Understanding and controlling of the surface wetting has a significant impact on many fields of science. In particular, wettability is a fundamental property of implant surface, which influences the initial cell adhesion [1]. With the development of modification technologies of biomaterials surfaces, the field of the coating fabrication has been broadened, from the wet-chemical deposition to the physical deposition [2, 3].

Radio-frequency (RF) magnetron sputtering is a known method for producing pure hydroxyapatite (HA) [4, 5] as well as HA with different admixtures, such as Si [6] or Ag [7]. Although RF-magnetron sputtering was widely used for fabrication of HA-based coating, the number of reports related to the wetting of the surface of HA thin film and influence of the surface topography on wettability is limited. It is known, that predefined topography can affect surface wettability. Recently, hydrophobic surface of silicate containing HA (Si-HA) film with 0.5 mol of silicate has been fabricated [6]. The deposited film was hydrophobic as a result of the formation of the nanostructured surface. The field of
new biomaterials development, particularly fabrication of multiscale surfaces, has progressed tremendously during the last years. Recent studies revealed that the combination of the multiscale (micro- and nanoscale) structures of implant surfaces with the predetermined chemical composition plays a crucial role in achieving the desired biocompatibility [8].

The aim of this study is to examine the role of the surface structure of pure HA and Si-HA-based coating fabricated via RF-magnetron sputtering on wetting characteristics.

2. Materials and methods

The HA coatings were deposited on the grounded Ti substrates via RF (13.56 MHz) magnetron sputtering. The deposition parameters were reported elsewhere [4]. The resulting coating thickness was determined by ellipsometry. A powder of Si-containing HA (Ca$_{10-x}$(PO$_4$)$_6$(SiO$_4$)$_x$(OH)$_2$, $x=0, 0.5$ and 1.72) was prepared by mechanochemical activation and then used as a precursor to prepare a target for sputtering. The mixture was slowly compacted in a press at the pressure of 70 MPa. The pressed powder was sintered in air at 1100°C for 1 h. The submicrometer structure of Ti was produced via acid etching (AE) and pulsed electron beam (PEB) treatment. The detailed information of treatment procedures was reported elsewhere [4].

Surface measurements at the nanoscale were evaluated using an atomic force microscope (AFM) Solver P47-PRO (NT-MDT, Moscow, Russia) in contact mode. An X-ray diffractometer (PANalytical, MA, USA) with Cu K$_\alpha$ radiation operated at 40 kV and 40 mA was used to characterize the coatings. The samples were scanned for 20 from 5° to 100° with a step size of 0.05° using grazing incidence X-ray diffraction (GIXRD) with an incident beam angle of $\Phi = 1.0°$. To calculate an average crystallite size and lattice parameters, Rietveld refinement (using the Le Bail method) with the program package TOPAS 4.2 from Bruker was performed. For each Rietveld refinement, the instrumental correction as determined with a LaB$_6$ standard powder sample from NIST (National Institute of Standards and Technology) as the standard reference material (SRM 660b). HA (#4-0432) and Ti (#44-1294) patterns from the ICDD database were used as references.

Contact angle analyses were performed with an optical contact angle apparatus (OCA 15 Plus Data Physics Instruments GmbH, Germany) using the SCA20 software (Data Physics Instruments GmbH, Germany). The static captive bubble method was chosen to measure contact angle. Five independent measurements have been realized on surface of each sample and the mean values were calculated.

3. Results and discussion

It was noted that Si addition, under the same deposition conditions, has influenced the coatings morphology. It is well-known that the surface morphology of the microstructures strongly depends on the content of dopants. Figure 1 shows AFM morphological images of the pure HA and Si-HA films.

In the case of HA-based film deposited on acid etched Ti, many grains ranging from 200 to 900 nm are observed on the surface. The grains can be either separated from each other or overlapped. 3D AFM images have revealed that Si-HA film deposited on acid etched Ti presents grains with dimensions ranging between 70-100 nm which are densely built into conglomerate formation (Figure 1). The surface roughness is the key factor to affect the hydrophobicity [9].

Figure 2 shows the typical XRD patterns of pure HA and Si-containing HA films. The diffraction peaks for pure HA and Si-HA ($x=0.5$ mol) can be indexed as hexagonal HA. No other diffraction peaks for any secondary crystalline phases were found. Moreover, the peaks of Si-containing HA coatings were slightly shifted to lower angles compared to that of the undoped HA coating. As shown in Figure 3, it can be an evidence of replacement of phosphate ions with silicate ions. However, for the samples doped with either 0.5 or 1.72 mol Si the intensity of HA peaks decreases.
Figure 1. 3D AFM images of the pure and Si-containing HA coatings deposited on Ti substrate with different initial morphology obtained using AE and PEB: a) HA coating on Ti after PEB; b) Si-HA (x=0.5 mol) coating on Ti after PEB; c) Si-HA (x=1.72 mol) on Ti after PEB; d) HA coating on Ti after AE; e) Si-HA (x=0.5 mol) on Ti after AE; f) Si-HA (x=1.72 mol) on Ti after AE.

The effect of Si doping on the structural changes such as the lattice parameters, unit cell volume and average crystallite size was analysed. The lattice parameters are estimated from the XRD peaks positions and refined using Rietveld analysis. The lattice parameters (a, b, c), unit cell volume (V), and average crystallite size calculated for different Si content in HA are summarized in Table 1.

The lattice parameters of undoped HA film were \( a = 9.451(2) \, \text{Å} \) and \( c = 6.901(2) \, \text{Å} \). For Si-containing HA films, the lattice parameters are slightly higher than that of undoped HA film. The lattice parameters and volume increases with increasing Si content in the film. The modification observed in the unit cell’s volume could be attributed to the differences in the ionic radii. The calculated crystallite size was found to decrease with increase of Si content. The average crystallite size was found to be 27 nm for undoped HA film and 17-20 nm for the Si-containing HA films, which indicated their nanocrystalline structure.
Figure 2. XRD patterns of the pure HA and Si-containing HA coating deposited on Ti after PEB treatment

Table 1. Lattice parameters, unit cell volume and crystallite size estimated for the coatings deposited via RF magnetron sputtering.

| Film                | Lattice parameters, [Å] | Crystallite size, [nm] | V, [Å³]   |
|---------------------|-------------------------|------------------------|-----------|
| HA                  | a = 9.451(2)            | 27±1                   | 533.8(3)  |
|                     | c = 6.901(2)            |                        |           |
| Si-HA, x=0.5 mol    | a = 9.482(3)            | 20±1                   | 539.4(4)  |
|                     | c = 6.927(3)            |                        |           |
| Si-HA x=1.72 mol    | a = 9.538(5)            | 12±1                   | 547.3(3)  |
|                     | c = 6.947(5)            |                        |           |

The average water contact angles on Ti after AE and PEB treatment were determined as 138.9° and 91.8°, respectively, exhibiting hydrophobicity. The static contact angle measurements demonstrated that, among all other films studied, pure nanocrystalline HA coating revealed the lowest contact angle. In figure 3 the Si-HA-based (x=1.72 mol) film revealed a higher water contact angle of 143.2 and 150° for PEB and AE Ti surfaces, respectively, showing hydrophobic surface. These results are in good agreement with that of the recent study [6]. It was reported that the wettability of the Si-HA (x=0.5 mol) coating is time-dependent with a tendency to become more hydrophilic over time.

An interesting fact of the influence of the substrate topography on the growth mechanism and, therefore, morphology and mechanical features of the HA-based coating is reported [4]. Wetting of the structured surface can be described using two distinct modes [10]. In the first mode, a rough surface is completely wetted by a liquid, known as a Wenzel state [11]. The apparent contact angle is described in this case via the Wenzel equation:

\[ \cos \Theta^* = r \times \cos \Theta \]  

where \( r \) is the roughness factor, defined as the ratio of the actual surface area and the projected surface area of the solid.
The Wenzel equation indicates that the roughness can amplify the wettability of a surface. If the surface is intrinsically hydrophobic, roughness will further enhance the surface hydrophobicity. In the case of the coated surface, a water droplet on the deposited film is expected to penetrate into the microscale grooves. However, air gaps are present in the nanoscale structure, thus forming a partial wetting state. Water sealed in microscale structure of Ti surface, resulting in strong adhesion between the surface and a liquid.

4. Conclusions
The morphology and composition of RF magnetron sputter-deposited HA coating fabricated on Ti were characterized using AFM and XRD. AE and PEB-treatment of Ti substrates and silicate content in the deposited HA films resulted in the different morphology of the coatings at micro- and nanoscale structures. The influence of micro- and nanoscale geometrical structures on wettability of the HA- and Si-HA-based was investigated. Water contact angles for the HA coated Ti samples were evaluated as a combined effect of micro roughness of the substrate and nano roughness of the HA films resulting in higher water contact angles compared with acid-etched (AE) or pulse electron beam (PEB) treated Ti substrates.

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