Investigation of the HA film deposited on the porous Ti6Al4V alloy prepared via additive manufacturing

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Abstract. This study is focused on the use of radio frequency magnetron sputtering to modify the surface of porous Ti6Al4V alloy fabricated via additive manufacturing technology. The hydroxyapatite (HA) coated porous Ti6Al4V alloy was studied in respect with its chemical and phase composition, surface morphology, water contact angle and hysteresis, and surface free energy. Thin nanocrystalline HA film was deposited while its structure with diamond-shaped cells remained unchanged. Hysteresis and water contact angle measurements revealed an effect of the deposited HA films, namely an increased water contact angle and contact angle hysteresis. The increase of the contact angle of the coating-substrate system compared to the uncoated substrate was attributed to the multiscale structure of the resulted surfaces.

1. Introduction
Additive manufacturing (AM) of plastics and metals is already well-established method in engineering and technology and is commonly used for rapid prototyping and small series production as well as manufacturing of the unique components with complex 3D shapes [1]. One of the rapidly growing application areas of the AM is medicine, especially orthopedics and prosthetics. These applications are utilizing strongest advantages of the AM technologies such as freedom of component shapes, possibilities of computer optimization of the manufactured-to-be component functionality and properties, and reasonable prices in case of manufacturing of small series of products. These benefits are already recognized by medical implant manufacturers and practical surgeons [1].

It is known that calcium-phosphate (CaP) coated titanium implants have been widely used in orthopedic and dental fields due to their excellent biocompatibility attributable to the surface properties [2]. Radio frequency (RF) magnetron deposited hydroxyapatite-based (HA) coatings have become a promising candidates for the promotion of a faster and more effective titanium implant osseointegration at early implantation times [3, 4]. In this study, the focus is based on the use of RF-magnetron sputtering to modify the surface of porous Ti6Al4V alloy fabricated via AM.

2. Materials and methods
All the samples used were fabricated using Ti6Al4V ELI powder (Arcam AB) in ARCAM A2 EBM® machine (Arcam AB, Mölndal, Sweden) [5]. All flat coin like sample had a dimension of 10 and 30 mm in diameter had flat surfaces normal to the melt layer surface and were made in a single
batch. Porous 3D-lattice scaffolds were made in two different batches with identical parameter settings and same diamond-shaped basic lattice cells. All samples were carefully blasted in the ARCAM powder recovery system using the same precursor powder. Electrochemical etching was carried out at 30° C in the ethanol and 2-propanol solution of the aluminum chloride and zinc chloride with the stabilized DC current density 0.2 A/cm² [6].

A powder of HA (Ca₁₀(PO₄)₆(OH)₂) was prepared using mechanochemical activation and then used as a precursor-powder to prepare a target for sputtering (Prof. M. Chaikina, Institute of Solid State Chemistry and Mechanochemistry SB RAS). The RF-power (500 W), argon gas pressure (working pressure 0.4 Pa, base pressure 10⁻⁴ Pa) and the distance between the target and substrate (40 mm) were kept constant in all experiments. HA coatings were deposited for 8 hours which resulted in the coating thickness of 700 nm.

The phase composition and the structure of the coatings were identified by X-ray diffraction (XRD-7000, Shimadzu, Japan) with CuKα radiation (λ=0.154 nm) in the 2θ range from 10° to 60° with a scan speed of 2.0°/min, sampling pitch of 0.03°, preset time of 5.0 sec at 30 kV and 30 mA. The average crystallite size was determined using the Scherrer’s equation from the broadening of the diffraction peaks taking into account the instrumental broadening and with the PowderCell 2.4 software. An instrumental broadening of 0.14 in 2θ was determined by the full width at half maximum of a silicon powder. As references for the patterns of HA and Ti #9-0432 and #44-1294 (ICDD database) were used, respectively. The morphology of the HA-coated samples was observed with the field-emission scanning electron microscopy (FESEM, Quanta-200, FEI, USA) equipped with an Energy Dispersive X-ray (EDX) system. 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 contact angle (CA) of water in air was measured using a sessile drop method. A minimum of 10 droplets (2 µL, 5 µL·s⁻¹) of water, 3 droplets of diiodomethane or ethylene glycol were examined for each sample, and the resulting mean CA values were then used for the calculations. The surface free energy σ was calculated using Owens-Wendt-Rabel-Kaelble (ORWK) method.

3. Results and discussion
Figure 1 illustrates the morphology of the Ti6Al4V alloy cellular structure with diamond-shaped unit cells. Unit cells dimensions demanded by the design were 500 µm with start diameter of 150 µm, but the resulting ones are some larger. As clearly visible from these images metal surface contains a number of powder grains attached to the bulk metal (figure 1b) providing a micrometer scale roughness, a feature commonly met for the powder bed AM processes. Surfaces are also showing distinct roughness at the sub-micron scale (figure 1c).
Figure 1. SEM images of the porous Ti6Al4V sample morphology prepared via AM. Images are acquired using both SE (b, c) and BSE (a) detectors

It has been extensively reported that the microscale morphology significantly influences cell behaviour such as adhesion, proliferation and differentiation in vitro and in vivo [7].

Figure 2 a. illustrates the morphology and composition of HA films prepared on the surface of Ti6Al4V substrates fabricated via AM technology. It can be seen that the surface of the HA-coated substrate is some smoother compared to that of uncoated Ti6Al4V. As already mentioned elsewhere [8], the initial island nucleation of the thin film was attributed to the preferred growth in the valleys. The authors observed that for a smooth and rough substrate, the film surface gets smoother with the increasing in the film thickness due to the preferred growth of the film in the valleys [8].

It was reported that the coating composition and thickness are strongly depended on the substrate that was used [9]. It has been also shown [10] that pretreatment of the titanium substrates can strongly influence the coated surface properties. A comparison of the HA films on titanium substrate surfaces modified by acid etching and pulse electron beam treatment revealed significant differences in the morphology of the films (roughness, grain size and shape) and the mechanical properties [10].

Figure 2. SEM image (a) and EDX spectrum (b) of the HA-coated Ti6Al4V prepared via AM

The Ca/P ratio of the CaP coatings deposited via RF-magnetron sputtering onto the Ti6Al4V substrate prepared via AM technology according to EDX-data was 1.20±0.03, which is lower than that of the 1.67 Ca/P ratio of stoichiometric HA (figure 2b).

The typical XRD-pattern of the HA coating fabricated via RF-magnetron sputtering on the surface of titanium prepared via AM is shown in figure 3.
All diffraction peaks corresponded to the structure of HA, no diffraction peaks from other phases were detected. HA coating showed a nanocrystalline structure with the crystallites of an average size of 32±9 nm. Normally, the most intense peaks of HA are observed in the 30–35° 2θ range. The lattice parameters of the HA coating deposited on the surface of porous titanium alloy were determined to be a=9.4042 and c=6.8875 Å.

The data presented in Table 1 show that HA coating deposited on the surface of porous Ti6Al4V alloy resulted in increase of the CA. It should be noted that water CA did not reveal any significant effect from the coating. Surface energy of the Ti6Al4V porous alloy was decreased after deposition of the HA coating. Previously, we observed increase of the water CA of the coating on titanium in case of the silicate-substituted HA prepared at different bias [11].

### Table 1. Surface wettability of Ti6Al4V porous alloy with and without HA coating

| Sample           | CA (degrees) | CA hysteresis (degrees) | Surface free energy (mN·m⁻¹) |
|------------------|--------------|-------------------------|------------------------------|
|                  | Water        | Water in 5 min          | diiodomethane               | ethylene glycol | dispersive | polar | total     |
| Bare Ti6Al4V     | 106±1        | 88±1                    | 34±1                        | 42±2             | 20±3       | 48.75 | 0.32   | 49.07     |
| HA-coated Ti6Al4V| 109±2        | 101±1                   | 56±2                        | 80±1             | 24±3       | 29.20 | 0.02   | 29.22     |

The increase of the CA of the coating-substrate system compared to the uncoated substrate was attributed to the hierarchical organization of the resulting surfaces. Thus, to study the process of surface wettability of a porous Ti6Al4V substrates a water droplet was placed and contact angle was monitored for a 5 minute time interval with a 1 minute step. It can be seen that in case of the coated substrates the water CA decreases slower than for the uncoated substrates. This allows to suggest that HA coating prevents water spreading over the surface of the porous Ti6Al4V alloy. Most probably it is because the water is becoming trapped in the microscale cavities of the surface of HA-coated titanium Ti6Al4V alloy resulted in a strong adhesion between the surface and a liquid.

### 4. Conclusion
RF-magnetron sputtering provides the ability to deposit thin HA coatings onto the surface of porous Ti6Al4V scaffold with the diamond lattice structure fabricated via AM. The HA coating showed a nanocrystalline structure with the crystallites of an average size of 30 nm. The lattice parameters of the HA coating prepared on the surface of porous titanium alloy were determined to be a=9.4042 and c=6.8875 Å. Water contact angle and hysteresis increase was revealed as an effect of the deposited HA films. Surface energy of the Ti6Al4V porous alloy was decreased after deposition of the HA coating. We attributed the increase of the contact angle of the coating-substrate system compared to the uncoated substrate to the multiscale structure of the resulted surfaces. Water sealed within the microscale structure of HA-coated titanium alloy surface resulted in a strong adhesion between the surface and a liquid.

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