

Additive manufactured Ti6Al4V scaffolds with the RF-magnetron sputter deposited hydroxyapatite coating

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Abstract. Present paper reports on the results of surface modification of the additively manufactured porous Ti6Al4V scaffolds. Radio frequency (RF) magnetron sputtering was used to modify the surface of the alloy via deposition of the biocompatible hydroxyapatite (HA) coating. The surface morphology, chemical and phase composition of the HA-coated alloy were studied. It was revealed that RF magnetron sputtering allows preparing a homogeneous HA coating onto the entire surface of scaffolds.

1. Introduction

Modern additive manufacturing (AM) is already using a wide variety of very different materials including metals. One of the key advantages of AM technologies is the freedom of three-dimensional shapes of manufactured components. One of the application areas where the advantages of additive manufacturing can be successfully used is biomedicine. In particular this technology allows for better operation planning and manufacturing functionalised implants specifically fit to the particular clinical case [1-3]. Metallic additively manufactured implants can also successfully replicate the complex microstructure of the substituted bones by integrating porous sections into monolithic implants improving the implant integration process and its long term stability in the body [3-5]. In many cases, when materials used for the metallic implants manufacturing are bioinert additional surface coatings can significantly improve the osseointegration [6-9]. But achieving homogenous coatings of the surfaces for the components with a complex three-dimensional structure, and especially the ones containing porous and 3D-lattice structures is quite challenging. Present work is devoted to the investigation of the morphology and phase composition of the coatings based on hydroxyapatite (HA) deposited on Ti64 scaffolds by RF-magnetron sputtering.

2. Materials and methods

Test samples containing solid and porous sections (made as 3D-lattices with regular lattice cells) were manufactured from titanium alloy Ti6Al4V by the Electron Beam Melting technology in ARCAM A2 EBM[®] machine (Arcam AB, Mölndal, Sweden) [10, 11] using manufacturing parameter settings recommended by the machine manufacturer.

Hydroxyapatite (HA) with a specific stoichiometric composition $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ was selected as a material for coating.

A HA powder was prepared in a mechanochemical activation process and then used as a precursor to prepare a target for magnetron-based sputtering. Critical sputtering parameters such as radiofrequency power (400 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. The



HA coatings were deposited for 8 hours which resulted in the coating thickness of 700 nm. Sputtering equipment was described in detail earlier [12].

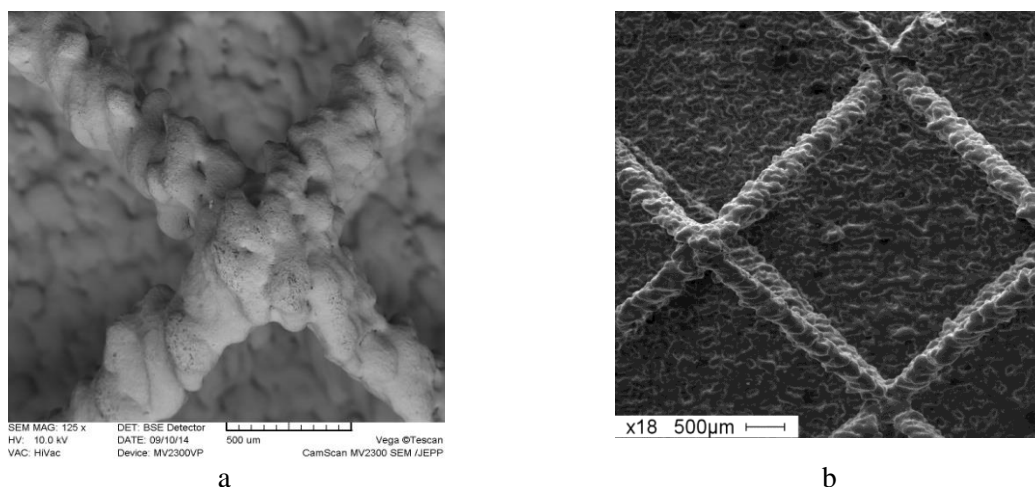
The phase composition and the structure of the coatings were identified by X-ray diffraction (XRD-7000, Shimadzu, Japan) with CuK α radiation ($\lambda=0.154$ nm) in the 2θ range from 10° to 60° with a scan speed of $2.0^\circ/\text{min}$, sampling pitch of 0.03° , preset time of 5.0 sec at 30 kV and 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 with the help of PowderCell 2.4 software. An instrumental broadening of 0.14 in 2θ was determined by the full width at half maximum of a calibration silicon powder. The database patterns #9-0432 and #44-1294 (ICDD database) were used for the pure HA and Ti respectively. The micro scale morphology of the samples was observed with SEM (CamScan MV2300 SEM, Great Britain) and field-emission SEM (FESEM, Quanta-200, FEI, USA) equipped with an Energy Dispersive X-ray (EDX) system.

3. Results and discussion

The RF-magnetron sputtering of the HA coating on the different rough surfaces offers the opportunity to create conformal coatings on the substrates that have specific surface features, without significantly changing the underlying microtopography [12, 13]. But the majority of the studies were performed with relatively planar sample surfaces. But it was unclear if the magnetron coating of the structures with multi-layer lattice structures backed by the solid parts suggested for the new generation implants [4, 5] would be at all effective. One of the serious concerns was due to the fact that electric fields in the conductive lattices drops dramatically when moving from outer to inner layers, which can completely prevent the coating of the deeper structure layers with the electrochemical and plasma-based methods.

Typical microscopy images of the surface of the lattice parts of the samples fabricated by EBM[®] before and after deposition of biocompatible HA coatings are shown in figure 1. The figure 1a shows 'the view from the top' of few cellular structure layers backed by the solid section of 'as manufactured' sample before coating. In the case of implants solid inner core of the structures should provide the mechanical integrity, and outer lattice layers should improve the biocompatibility promote the bone ingrowth for better implant fixation in the body. In present experiments low density regular lattice with diamond-shaped cells 5×5 mm and starts thickness of 0.35 mm were used.

As illustrated by the images in figure 1 resulting HA coating is quite conformal and well replicates the original surface features of the lattice with some smoothing of the smallest features in their microstructure. The same time the surface of the coating has its own microroughness, which can also be beneficial for the osseointegration.



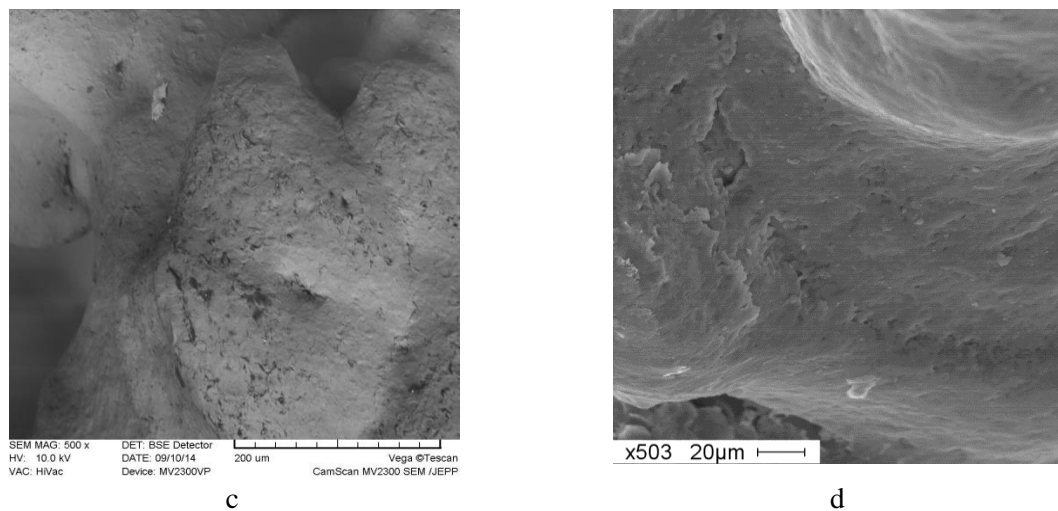


Figure 1. SEM image of Ti64 mesh composite before (a, c) and after the coating (b, d)

Coated samples were investigated to identify the properties of the HA coating on the struts of the lattice scaffolds (figure 2). The boundary of the HA coating layer can be easily visible on the broken struts of the lattice structure. Cutting and polishing of such structures for the analysis of the coatings is quite challenging, as many of easily available methods either contaminate the samples or overheat them. Thus careful mechanical braking provides easy alternative for the express analysis of the lattice structure elements.

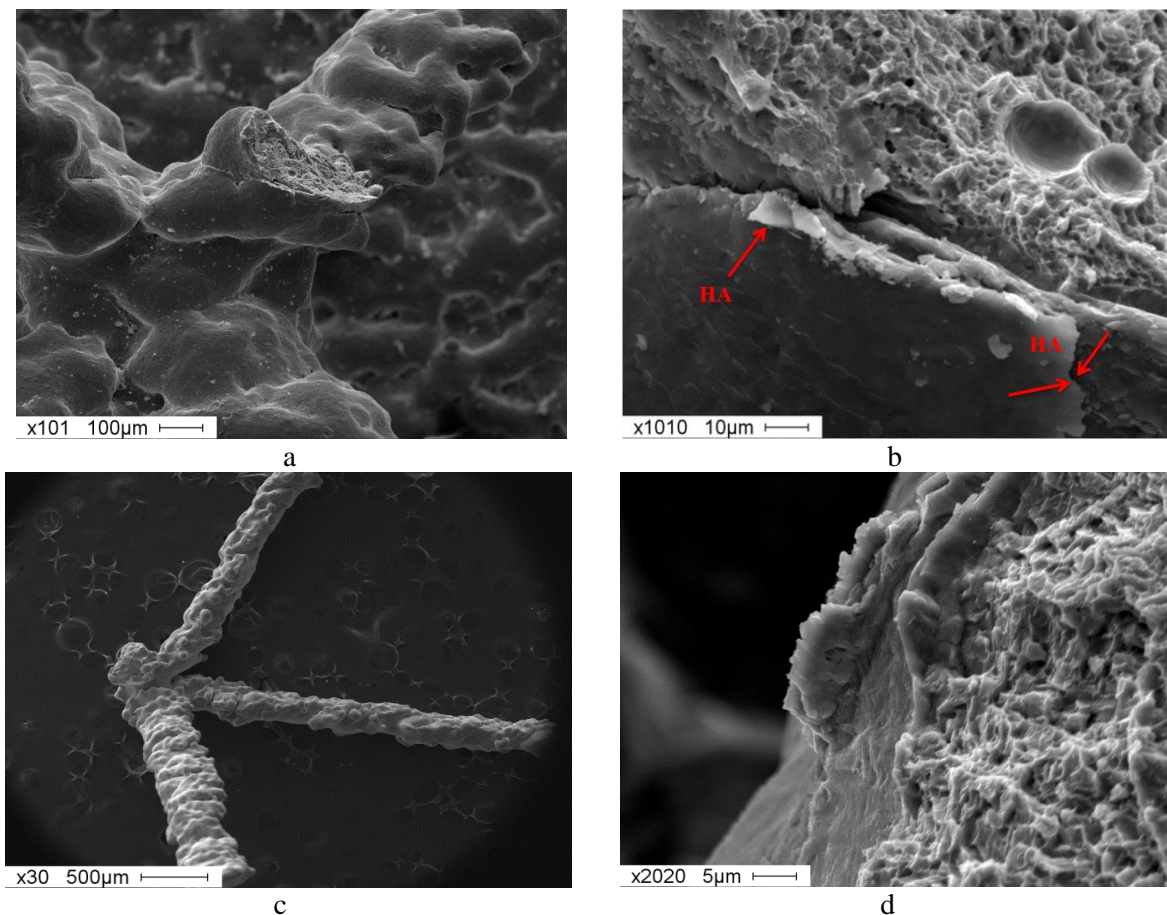


Figure 2. SEM image of the HA coated Ti6Al4V 3D-lattice structures prepared by additive

manufacturing in EBM[®] technology. The HA coating is shown by arrows.

A typical EDX spectrum of the HA-coated scaffold is shown in figure 3. The study showed the presence of elemental composition on the surface of Ca, P, C and O. The high concentration of carbon on the coated surfaces appears after cutting and most probably results from the sample contamination.

Since the EDX-technique is a semi-quantitative method, it is not possible to reveal a true Ca/P ratio for the coating. However, the calculated value of the Ca/P ratio in the case of the coated substrates was 1.0 ± 0.1 . According to the XPS results presented in our previous study, the Ca/P ratio for nanocrystalline HA coatings deposited via the RF magnetron sputtering technique with comparable process parameters was reported in the range of 1.65–1.86 [14, 15].

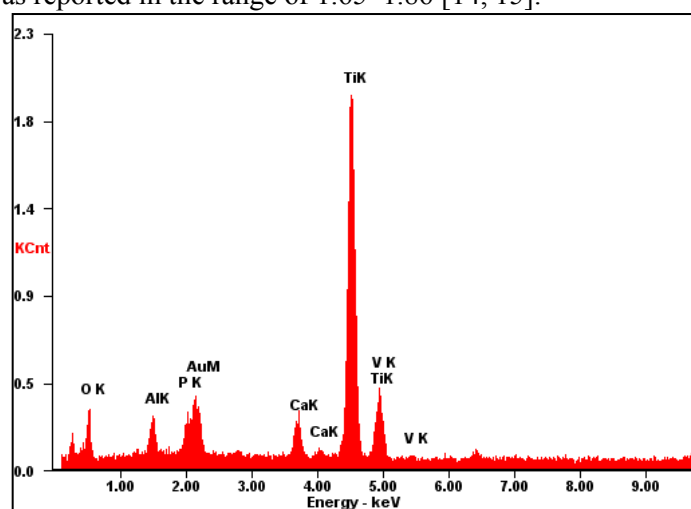


Figure 3. EDX spectrum on surface of the titanium scaffold coated with HA

The structure and phase composition are important characteristics having a decisive influence on the functional properties of the coatings.

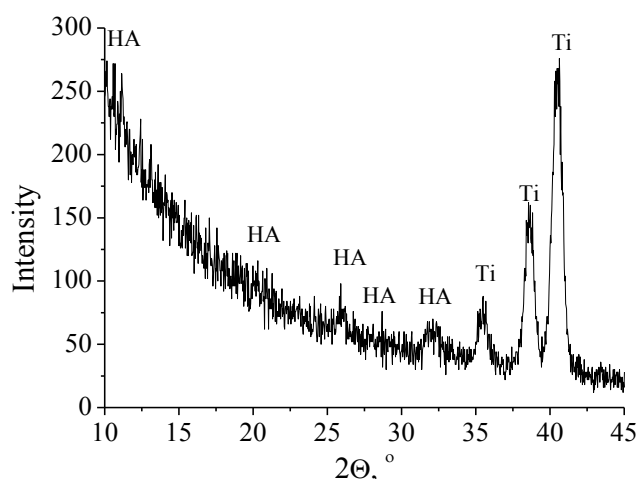


Figure 4. XRD pattern of the HA-coated titanium alloy prepared via additive manufacturing

The typical XRD-pattern of the HA coating fabricated via RF-magnetron sputtering on the surface of Ti64 alloy prepared via additive manufacturing is shown in figure. 4. The peaks at 25.9° (002), 31.8° (211), 32.2° (112), 32.9° (300) correspond to the diffraction pattern of the HA with hexagonal

crystalline structure. The most intense peak in the HA spectrum is at $31.8^\circ(211)$, but the second most intense one at $25.9^\circ(002)$ seems to have higher relative intensity as compared to the database values. Such phenomenon was also observed previously [16]. The parameters of the lattice $a = 9.4042$ and $c = 6.8875 \text{ \AA}$ correspond to the HA hexagonal arrangement (space group P63/m). The deposition mechanism of HA in magnetron-based method can be described as the formation of amorphous calcium phosphate clusters, their conversion into HA nanodomains and the crystallization of the grain domains with a preferential orientation along the HA [002] direction [17]. The magnetron sputtering plasma parameters have a great influence on the physicochemical and mechanical properties of the calcium phosphate films, and can be adjusted to produce single-phase HA films generated at a high deposition rate and high thermal stability [18].

4. Conclusions

Results of present studies indicate that additively manufactured metallic 3D-lattice structures can be effectively coated with hydroxyapatite using magnetron-based deposition methods. HA coating of the lattice elements is homogeneous and quite conformal but has certain smoothing effect hiding microstructure of the original metallic surfaces. The same time surface of the HA coatings has its own microroughness. Structural analysis of coatings indicates the hexagonal structure of HA, though the relative intensities of the corresponding peaks in the XRD spectra show some difference with the database values. Further studies should be carried out to identify the efficiency of magnetron-based method for the HA coating of dense 3D-lattice scaffolds, and the possibility to control the coating layer surface microroughness.

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