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ENGINEERING, ENVIRONMENT
AND MATERIALS IN
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JAHORINA
11th - 13th March 2019

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FACULTY OF TECHNOLOGY ZVORNIK**



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**“ENGINEERING, ENVIRONMENT AND MATERIALS IN
PROCESSING INDUSTRY”**

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**NOVEL *IN-SITU* SYNTHESIS OF HYDROXYAPATITE/TITANIUM OXIDE
COMPOSITE COATINGS ON TITANIUM BY SIMULTANEOUS
ANODIZATION/ANAPHORETIC ELECTRODEPOSITION**

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Abstract

In-situ synthesis of HAp/TiO₂ coating on titanium was performed via anaphoretic deposition of HAp and simultaneous anodization of Ti to produce highly adherent and strengthened composite coating. The prepared coatings were characterized by field emission scanning electron microscopy, X-ray diffraction and electron dispersive spectroscopy. HAp on anodized titanium was prepared at constant voltage of 60 V and deposition time of 45 s, which provided uniform and adherent HAp/TiO₂ composite coating on Ti. Since smaller size of HAp crystals within highly porous coating structures is of improved binding ability to various biomolecules, our coating is expected to be of excellent coverage and compactness. The obtained coating can be good candidate for bone implants due to reduced brittleness and improved adhesion.

Key words: *in situ anaphoretic deposition; hydroxyapatite coating; anodization; titanium oxide*

Introduction

Titanium is one of the few biocompatible metals that is being successfully and widely used for biomedical applications, mostly as dental and medical implants due to its appropriate hardness, adhesion, corrosion resistance, strength, toughness, density and low Young's modulus (Ahmadi, Mohammadi, & Sadrnezhaad, 2016; Ahmadi & Sadrnezhaad, 2016; Dezfuli, Sadrnezhaad, Shokrgozar, & Bonakdar, 2012; Geetha, Singh, Asokamani, & Gogia, 2009; Liu, Chu, & Ding, 2004; Long & Rack, 1998). However, it has been shown that titanium is not an fully applicable replacement for bone tissue due to differences in its physical and chemical characteristics relative to the bone, which causes poor osteoconductivity and osteoinductivity (Hamada et al., 2002; Han et al., 2017).

Nowadays, the enhancement of osteointegration and improvement of bone tissue regeneration over a titanium implant is subjected to modification of titanium surface by hydroxyapatite (HAp, Ca₁₀(PO₄)₆(OH)₂) (Niespodziana, Jurczyk, Jakubowicz, & Jurczyk, 2010). It is widely used in medical applications such as tissue engineering, drug delivery and bone tissue repair. HAp is of porous structure and sufficient bioactivity for its partial resorption leading to successful replacement of natural bone cells (Williams & D.F. Williams, 1987). It has the ability to create strong chemical bonds with bones.

Among all modification methods, anodization of the substrate surface prior to HAp deposition was proven to be a promising method for modifying the metal substrates (Ungureanu et al., 2016). This oxidation has attracted more attention due to its simplicity, low cost and excellent control even over the nanotube morphology of TiO₂ by changing anodization conditions. One of the most commonly used methods is the surface anodization in the acidic environment and electrodeposition of the bioactive HAp coating. Furthermore, the alkaline pretreatment of nanotubular titanium oxide layer (ATi) on implant surface has been shown to accelerate the formation of HAp, which has characteristics and structure mimicking the features of bone tissue (Parcharoen, Termsuksawad, & Sirivisoot, 2016). However, the literature data related to concurrent process of modifying the surface of the metal titanium substrate with the simultaneous application of the HAp coating can be hardly found, where such coating would have good adhesion to the substrate, or the coating itself would be incorporated into the substrate structure. Therefore, the aim of this work is to make an attempt of *in situ* synthesis of HAp/TiO₂ composite coating on titanium substrates *via* anaphoretic electrophoretic deposition of HAP and simultaneous anodization of Ti to strengthen the biocompatible composite coating without need for sintering of coating.

Experimental Part

A chemical precipitation method was used to prepare hydroxyapatite powder by the reaction of calcium oxide (obtained by calcination of CaCO₃ for 5 h at 1000 °C in air) and phosphoric acid. A stoichiometric amount of the calcium oxide was stirred in distilled water for 10 min and phosphoric acid was added drop wise to the suspension in order to obtain hydroxyapatite powder, Ca₁₀(PO₄)₆(OH)₂. When all the necessary quantity of phosphoric acid was introduced, the pH reached a value of 7.4–7.6. The obtained suspension was heated to 94 ± 1 °C for 30 min and stirred for another half an hour. Upon sedimentation, the upper clear solution layer was decanted. The suspension was then spray-dried at 120 ± 5 °C into granulated powder (Eraković et al., 2013).

For anaphoretic deposition the HAp suspension was prepared by dissolving 1.0028 g of nanosized HAp powder in 100 mL of absolute ethanol with added 10 wt.% NaOH and pH value of 10. Subsequently, suspension was ultrasonicated for 15 min to reach homogeneous and stable state. The titanium plates (dimensions: 10 mm × 10 mm × 0.89 mm, for surface analysis, Aldrich, 99.7 % purity) were used as substrates for anaphoretic deposition of HAp coatings. Before deposition, Ti plates were mechanically pretreated. Metal plates were polished with different grades sandpaper, followed by wet polishing with 0.3 μm and 0.05 μm alumina and then washed in ethanol for 15 min in an ultrasonic bath.

A two-electrode cell arrangement was used for anaphoretic electrodeposition. The working electrode was a titanium plate, and the counter electrode was Winkler type platinum electrode, placed around working electrode at the smallest distance of 1.5 cm. The electrochemical cell was filled with HAp/NaOH suspension and purged with N₂ for 30 min. A Hewlett Packard HP6024A potentiostat/galvanostat was used as power supply. Prior to anaphoretic depositions, the HAp suspension was ultrasonically treated for 30 min to obtain a homogeneous particle distribution and the suspension was stirred for 2 h by magnetic stirrer, and the HAp suspension was constantly stirred during anaphoretic deposition. The HAp/TiO₂ (anHAp/TiO₂) composite coatings on Ti were obtained at constant voltage of 60 V for a deposition time of 45 s, at room temperature. AnHAp/TiO₂ coatings were air dried at room temperature.

Surface morphologies of obtained anHAp/TiO₂ coating and titanium surface were analyzed by field emission scanning electron microscopy (FE-SEM). Structural and phase composition was analyzed by X-ray diffraction (XRD).

Results and Discussion

Figure 1 shows SEM image with detailed morphology of anHAp/TiO₂ composite coating on titanium with needle-like and granular HAp shapes. It can be seen that deposition of

anHAp/TiO₂ took place and there are no visible cracks. The reason for this occurrence is most likely TiO₂ layer formation simultaneous with HAp deposition. The former statement was proven by XRD, which will be discussed later. From Figure 1 it can be seen that anHAp/TiO₂ coating consist of different particle shapes i.e. needle-like and granular. Granular particles are obtained by agglomerating growing needle-like particles, which are essentially starting HAp powder. Formation of HAp coating without cracks could be due to *in-situ* depositing of anHAp/TiO₂ coating and further investigation are done towards proving this statement.

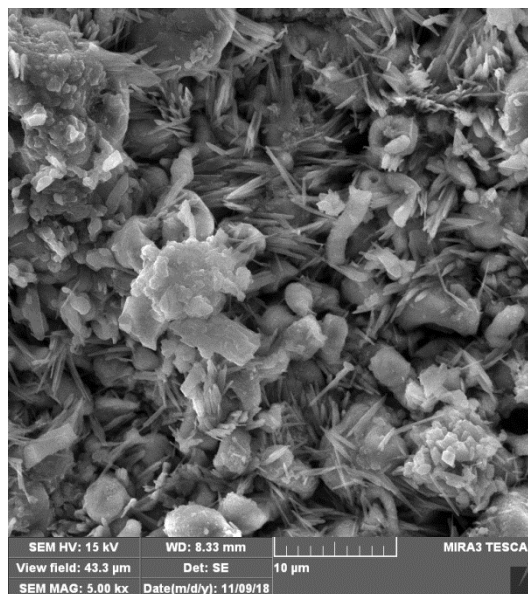


Figure 1. SEM microphotograph of anHAp/TiO₂ coating, magnification x5000

FE-SEM image of titanium surface after removing anHAP/TiO₂ coating is shown in Figure 2.

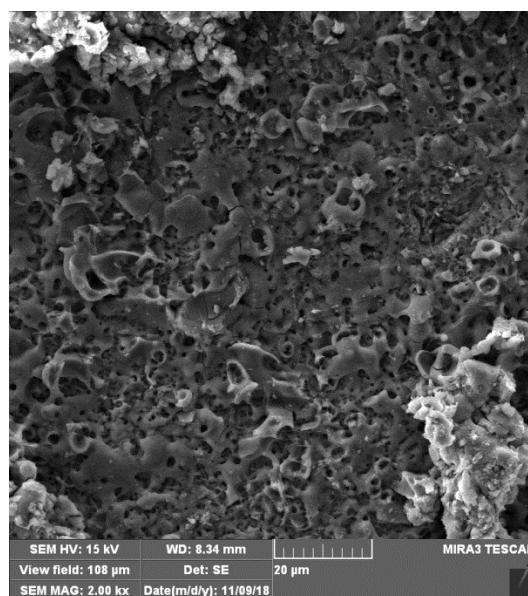


Figure 2. FE-SEM microphotographs of titanium surface after removing anHAP/TiO₂ coating

It can be seen from Figure 2 that morphology of Ti substrate of anHAP/TiO₂ coating is of tubular shape, and tube formation occurs mainly due to competing processes of anodization and electrophoretic deposition of HAp. During the anodization of Ti the evolution of O₂ takes place, forming tubular-like shapes on the surface. This evolution of O₂ is locally changing pH value at

the vicinity of the substrate, and two phases are formed. This local change of pH value damages negatively charged micelle of HAp powder and deposition of HAp onto the surface occurs. Since this process happen almost instantaneously and simultaneously the adhesion is improved. In order to confirm HAp and TiO₂ presence in composite anHAp/TiO₂ coating, XRD measurements were performed. Figure 3 shows XRD pattern of anHAp/TiO₂ coating, and specific phase analysis is discussed in the following paragraph.

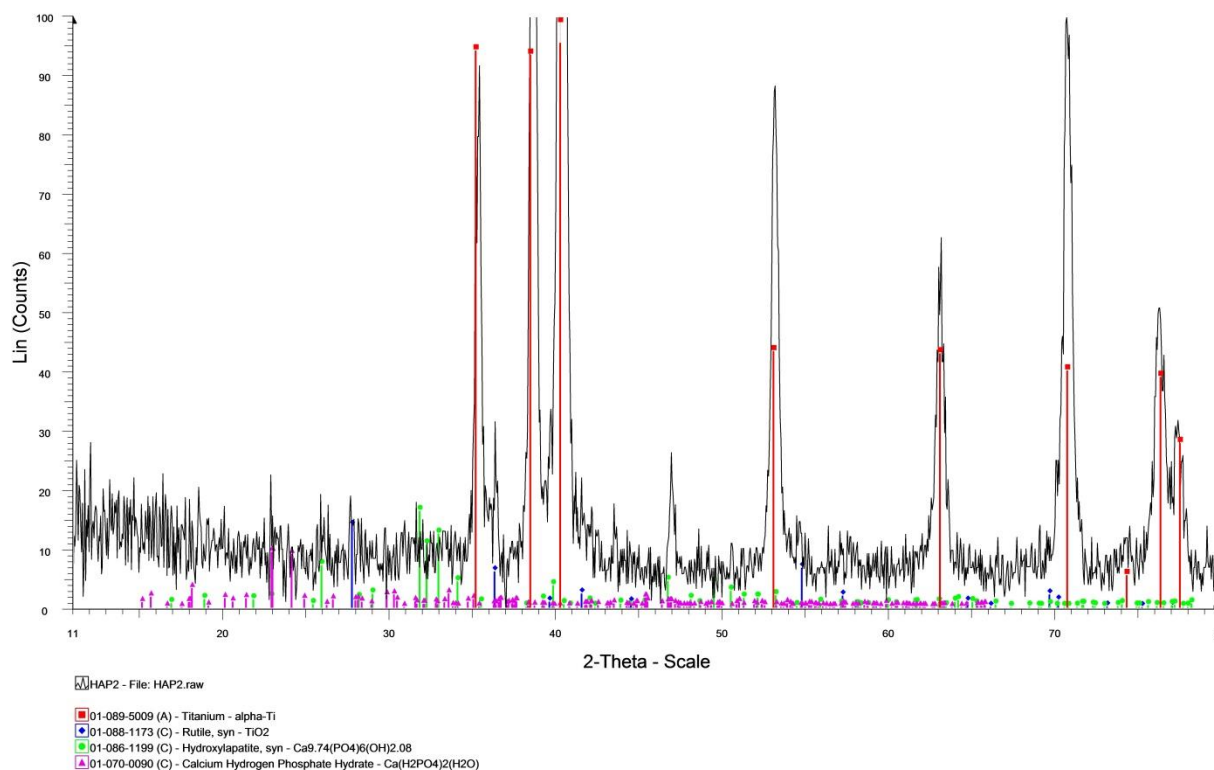


Figure 3. XRD diffractogram of anHAp/TiO₂ coating with specific phase analyses.

The diffractogram revealed characteristic peaks of hydroxyapatite related to crystal planes (002), (211), (112) and (300) at $2\theta = 25.85^\circ$, 31.60° , 32.25° and 33° , respectively (JCPDS standard XRD card No. 86–1199) although they are partially masked and of apparent low intensity due to dominating reflections from the Ti substrate. The most intensive peaks of the pattern were Ti peaks of the substrate (JCPDS standard XRD card No. 89-5009). Specific most intense XRD reflections of rutile TiO₂ at $2\theta = 27.85^\circ$, 36.35° and 54.80° (JCPDS standard XRD card No. 88-1173) are also seen, although they are also masked by Ti reflections. The presence of calcium phosphate phase was also indicated by the peaks at $2\theta = 22.85^\circ$ and 24.10° (JCPDS standard XRD card No. 70–0090). It is assumed that this phase is formed during deposition when the pH value is locally changed near the Ti surface and negatively charged micelle partially collapses. There is unidentified peak at $2\theta = 46.95^\circ$ which is also present at XRD diffractogram of pure Ti substrate.

Conclusions

Nano-hydroxyapatite coating has been successfully synthesized by novel *in situ* method of anaphoretic deposition on titanium substrate with simultaneous Ti surface anodization. The formation of hydroxyapatite coating was confirmed by Scanning Electron Microscopy and X-ray diffraction (XRD). anHAp/TiO₂ coating does not need sintering process, and simultaneous Ti anodization and HAp deposition occur, where HAp crystals incorporate in the anodized Ti surface. This means that TiO₂ is generated also on the Ti substrate simultaneously with HAp coating. From XRD results it could be concluded that the electrophoretic composite HAp

deposition has been successful due to appearance of hydroxyapatite diffraction peaks at $2\theta = 25.85^\circ$ and 31.6° . One can conclude that with appropriate experimental conditions and proper choice of electrolyte leading to stable negative HAp micelle excellent coverage of the surface can be obtained.

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