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Novel method for synthesis of biocompatible hydroxyapatite/passive oxide layer on modified titanium surface

Zoran Janković¹, Marijana R. Pantović Pavlović², Anto Gajić³, Veljko Marić⁴, Jasmina Stevanović², Sanja Eraković², Miroslav M. Pavlović²

¹V&Z Zaštita, d.o.o., Banja Luka, Republic of Srpska, Bosnia and Herzegovina

²University of Belgrade, ICTM-Department of Electrochemistry, Belgrade, Serbia

³Rudnik i termoelektrana Ugljevik, Republic of Srpska, Bosnia and Herzegovina

⁴University of East Sarajevo, Faculty of Medicine Foča, Republic of Srpska, Bosnia and Herzegovina

Abstract

Hydroxyapatite (HAp) is the most suitable biocompatible material for bone implant coatings. However, its brittleness is a major obstacle, and that is why, recently, research focused on creating composites. In this study, a novel in situ synthesis of HAp coating on titanium was presented. HAp was anaphoretically deposited from alkaline-ethanol suspension in one step process. Morphology of the coating was investigated by optical microscopy, while deposited HAp was characterized using ATR-FTIR. It was concluded that HAp has excellent coverage of the surface without delamination. The obtained coating can be good material for bone implants due to solving HAp brittleness.

Introduction

In recent years, new materials for use in orthopedic surgery have been the subject of extensive research. The main challenges of biological implants have an appropriate hardness, adhesion, biocompatibility and corrosion resistance. Titanium is one of a small number of biocompatible metals which has been successfully used as dental and medical implants, since it has advantageous properties such as strength, toughness, density, low Young's modulus, corrosion resistance and biocompatibility, which makes it suitable material for biomedical applications [1-6]. However, it was shown that titanium is not an ideal replacement for bone tissue due to differences in its physical and chemical characteristics in relation to the bone, which is reflected in poor osteoconductivity and osteoinductivity [7, 8]. On the other hand, the titanium can cause an adverse reaction of the body upon its implantation [9]. Although little of this problem is reported in the literature, there are isolated cases and studies to prove it.

In order to increase osteointegration and improve regeneration of the bone tissue on the implant, modification of titanium surface is required with a biologically active material. The most commonly used biocompatible material is a hydroxyapatite (HAp, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) [10]. Hydroxyapatite has the chemical structure that resembles bone mineral composition with similar release of Ca^{2+} и PO_4^{3-} ions and it can be used during the formation of new bone formation [11-13]. HAp has porous structure and due to its bioactivity HAp leads to its partial resorption and replacement of natural bone cells [14]. It has the possibility of creating a strong chemical bonds with bones.

The literature contains numerous methods for the synthesis of HAp. A microwave method leads to formation of suitable HAp coating with the composition and structure similar to bones [15-19]. HAp nucleation is favored by electrostatic binding with the hydroxyl groups of calcium ions [20, 21]. Many researchers have reported that in systems with polar molecules, microwave irradiation can be significantly speed up the chemical reaction by reducing the activation energy [22, 23].

Microwave hydrothermal method can be used as an alternative, which has been found to be suitable solution for preparation of the mesoporous HAp nanoparticles without the use of a template

(mold) [24, 25]. Another way of obtaining of hydroxyapatite is direct or indirect chemical deposition, and chemical precipitation method consists of the reaction between $\text{Ca}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{HPO}_4$, $\text{NH}_3 \cdot \text{H}_2\text{O}$ and $\text{C}_2\text{H}_5\text{OH}$, which forms HAp of controlled morphology and particle size [26].

Electrophoretic deposition (EPD) is another method of surface modification that is used for improving the bioactivity of the surfaces by deposition of calcium phosphate (CaP) particles on TiO_2 electrode under high voltage [27-29]. The advantages of this method are rapid formation of the coating, simple instrumentation, deposition of very pure stoichiometric coatings on complex surfaces. However, the EPD technique does not provide good adhesion of the coating to the substrate. For this reason, two step process - plasma electrolytic oxidation coupled with electrophoretic deposition - PEO-EPD for obtaining the porous hydroxyapatite coatings with incorporated particles of TiO_2 particles on titanium can be found in the literature. [29]. Electrolytic plasma oxidation is one the most useful methods for the surface modification of titanium since the porous and adherent coatings of nanotubular layer are obtained [29].

Due to major differences between the properties of the bioactive material and the metal substrate, adhesion of the coating to the substrate remains a major problem. During review of the literature it has been observed that most of the works dealing with a modification of the coating and the surface of the substrate without adhesion tests between them [7, 10, 29-31], nor adequate adhesion testing were performed which include mechanical testing [32]. The problem of poor adhesion of the coating appears in the form of delamination, poor mechanical properties and poor connections between the ceramic and metal. A potential solution to this problem is seen in the methods of surface modification of the substrate and/or HAp coatings in order to improve adhesion. Papers that have dealt with the adhesion of the coatings and substrate modifications [33-35] did not suggest a process which would, in the same time, modify the coating and substrate, regardless of the relatively positive obtained results of adhesion.

Spontaneous passive oxide layer of titanium is very sluggish and it takes a long time after implantation until osteointegration. The modification of the surface, thereof, leads to the increase in roughness of the implant surface, and hence adhesion of bioactive ceramic coating on a substrate [36]. Most of the titanium implants are treated with bioactive ceramic material, in order to improve biocompatibility, osteointegration and the adhesion of coatings on the substrate [36-38].

Anodizing the substrate surface has proven to be a promising method of modifying metals. One of the most commonly used method is the anodization of surface with simultaneous treatment in an acidic environment, and a bioactive electrodeposition of HAp coating. On the other hand, it was shown that pre-treatment of alkali nanotubular titanium oxides (ATi) accelerates the formation of HAp, having the characteristics and structure as the bone tissue [39]. Nanostructured HAp is formed on the pretreated and ATi ATi (P-ATi), in contrast with conventional Ti [39].

The aim of the work was novel process of *in situ* synthesis and characterization of anaphoretic hydroxyapatite coatings on modified titanium surfaces by anodization process.

Experimental

A chemical precipitation method was used to prepare hydroxyapatite powder by the reaction of calcium oxide (obtained by calcination of CaCO_3 for 5 h at 1000 °C in air) and phosphoric acid. A stoichiometric amount of the resulting calcium oxide was mixed and stirred in distilled water for 10 min and phosphoric acid was added dropwise to the suspension in order to obtain hydroxyapatite powder, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. When all the necessary quantity of phosphoric acid was introduced, the pH reached a value of 7.4–7.6. The obtained suspension was preheated to 94 ± 1 °C for 30 min and stirred for another half an hour. After sedimentation, the upper clear solution layer was decanted. The suspension was then spray-dried at 120 ± 5 °C into granulated powder [40]. HAp powder was then suspended in a solution containing 5 wt.% of NaOH with 50% of $\text{C}_2\text{H}_5\text{OH}$.

Electrochemical measurements were performed in a two-electrode cell. For this purpose, an electrochemical work station (Hewlett Packard HP6024A) having potentiostat/galvanostat provided with corrosion and physical electrochemistry software and a desktop computer (HP) was used. A platinum wire was used as counter electrode. The working electrode geometric area exposed to electrolyte was 0.39 cm^2 . The cell was filled with HAp suspension and purged with N_2 for 30 min prior to electrochemical measurements.

Morphology of the obtained HAp coatings was determined by optical microscope Olympus BX41. Fourier transform infrared spectroscopy (FTIR) was recorded on anodized titanium and on anaphoretic deposited HAp coating composite. Michelson MB Series Bomen FTIR was used (Hartmann Braun), scanning from 400 to 4000 cm^{-1} .

Results and discussion

In order to obtain *in situ* HAp coating and to compare it with pure Ti after anodization, two sets of experiments were performed, i.e. pure titanium anodization and anaphoretic HAp coating deposition from alkaline solution. For HAp to be anaphoretically deposited, it needs to be in a form of suspension with negatively charged micelle. Pure ethanol in 5 % NaOH was proven to be excellent solution of choice for this task, making HAp suspension stable for a long period of time. Both anodization and anaphoretic deposition were performed from 50-70 V at 0.5 mA in galvanostatic regime for 5 min. Obtained anodized titanium surface and deposited HAp coating are shown in Figure 1.

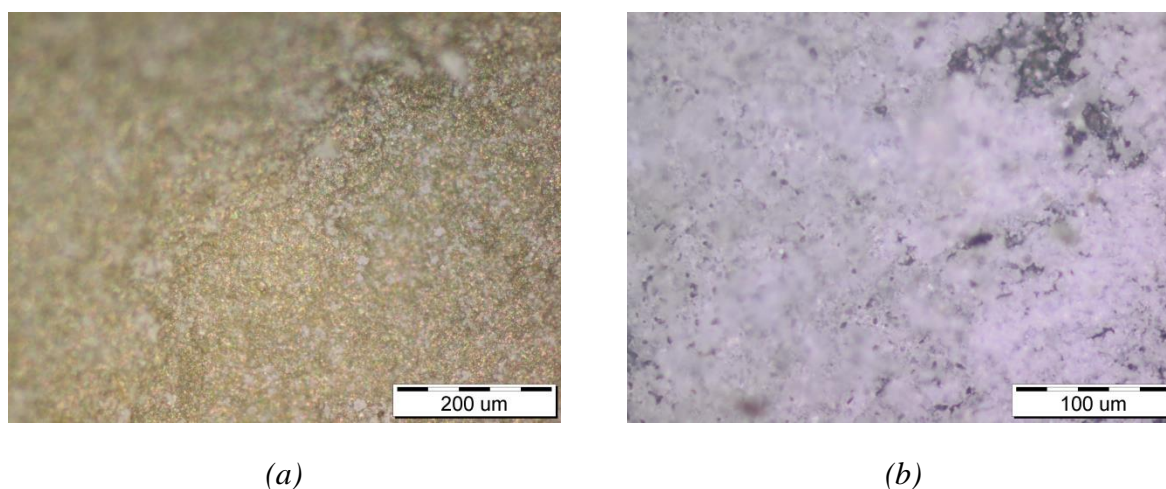


Figure 1. Optical images of (a) anodized titanium and (b) HAp coating on titanium.

It can be seen that HAp has excellent coverage of the surface with a firm deposit that is not delaminating. The obtained coating can be good material for bone implants due to solving HAp brittleness.

Further evidence of presence of HAp coating on titanium, and hence its functional groups is characterized by ATR-FTIR spectrum which is shown in Figure 2.

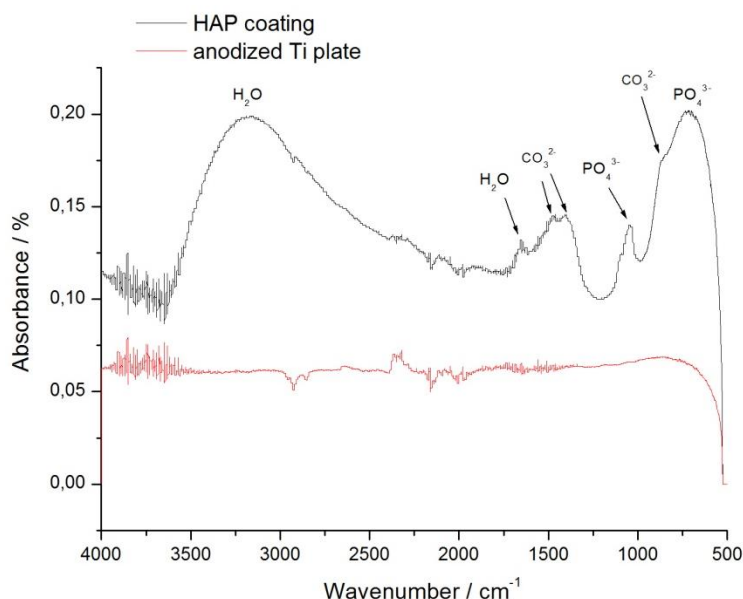


Figure 2. ATR-FTIR spectrum of anodized titanium (bottom red line) and HAP coating (top black line).

The spectra display typical PO_4^{3-} characteristic bands of hydroxyapatite coating. Two absorption bands were clearly distinguished at the following wave numbers 1041 and around 718 cm^{-1} in the ν_3 and ν_1 phosphate mode region. Additional weak bands at 872, 1402, and 1476 cm^{-1} are assigned to carbonate species (CO_3^{2-}) in the apatite lattice [41]. These peaks in the FTIR spectrum can be attributed to the reaction between CaO and CO_2 from the atmosphere. In the FTIR spectrum of HAP coating (Figure 2), the wide band at 3170 cm^{-1} is attributed to the OH stretching of H_2O molecules. The band at cca. 1650 cm^{-1} is from water (bending modes). The observed functional groups and their corresponding assignments are presented in Table 1.

Table 1. Some important functional groups assignments of HAP coating.

Wavenumber cm^{-1}	Stretching mode	Functional group
3170	Ion Stretching	$\text{H}_2\text{O}/\text{OH}^-$
1650	Out of plane bending mode	H_2O
1402, 1476	Asymmetric stretching	CO_3^{2-}
1041	Asymmetric stretching	PO_4^{3-}
872	Out of plane bending mode	CO_3^{2-}
718	Asymmetric bending vibration	PO_4^{3-}

Conclusions

Nano-hydroxyapatite coating has been successfully synthesized by novel *in situ* method of anaphoretic deposition on titanium substrate. The formation of hydroxyapatite coating was confirmed by optical microscopy and Attenuated Total Reflection Fourier transform infrared spectroscopy (ATR-FTIR). It can be concluded that with good preparation and proper choice of suspension medium leading to stable negative micelle HAP obtains excellent coverage of the surface with a firm deposit that is not delaminating. This coating has good properties to be used as a material for bone implants.

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