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**Radoje V. Pantovic**

**Zoran S. Marković**

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**IN SITU SYNTHESIS OF BIOCOMPATIBLE COMPOSITE LAYER  
OF HYDROXYAPATITE/PASSIVE OXIDE SURFACES ON  
THE MODIFIED TITANIUM**

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**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.

**Key words:** hydroxyapatite, anaphoretic deposition, titanium, FTIR.

**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  $\text{Ca}^{2+}$  и  $\text{PO}_4^{3-}$  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.

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  $\text{TiO}_2$  electrode under high voltage [15-17]. 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. 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, 17-19], nor adequate adhesion testing were performed which include mechanical testing [20]. 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 [21-23] 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.

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 [24]. Nanostructured HAp is formed on the pretreated and ATi ATi (P-ATi), in contrast with conventional Ti [24].

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  $\text{CaCO}_3$  for 5 h at  $1000\text{ }^\circ\text{C}$  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  $94 \pm 1\text{ }^\circ\text{C}$  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  $120 \pm 5\text{ }^\circ\text{C}$  into granulated powder [25]. HAp powder was then suspended in a solution containing 5 wt.% of NaOH with 50% of  $\text{C}_2\text{H}_5\text{OH}$ .

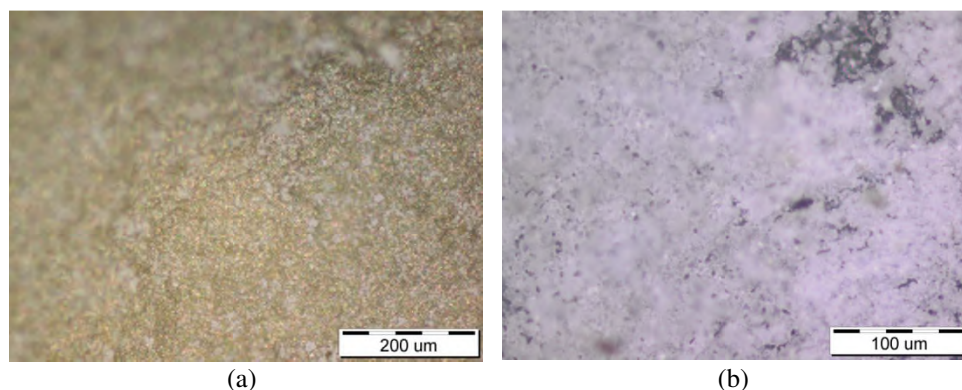
Electrochemical measurements were performed in a two-electrode cell. For this purpose, an electrochemical work station (Hewlett Packard HP6024A) having potentiostat/galvanostat provided with corrosion and physical electrochemistry software and a desktop computer (HP) was used. A platinum wire was used as counter electrode. The working electrode geometric area exposed to electrolyte was  $0.39 \text{ cm}^2$ . The cell was filled with HAp suspension and purged with  $\text{N}_2$  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  $4000 \text{ cm}^{-1}$ .

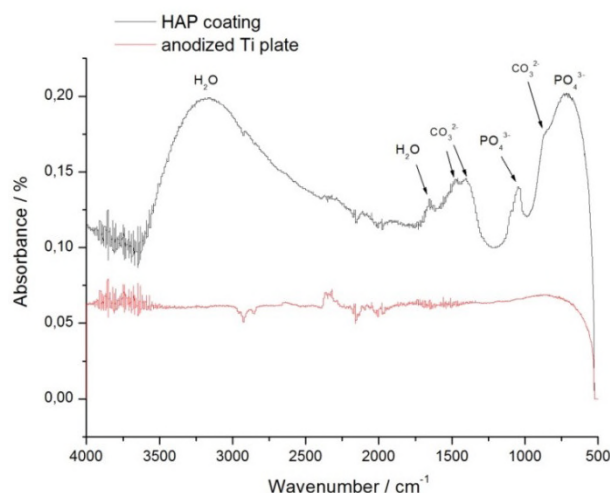
## RESULTS AND DISCUSSION

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  $\text{PO}_4^{3-}$  characteristic bands of hydroxyapatite coating. Two absorption bands were clearly distinguished at the following wave numbers 1041 and around  $718\text{ cm}^{-1}$  in the  $\nu_3$  and  $\nu_1$  phosphate mode region. Additional weak bands at 872, 1402, and  $1476\text{ cm}^{-1}$  are assigned to carbonate species ( $\text{CO}_3^{2-}$ ) in the apatite lattice [26]. These peaks in the FTIR spectrum can be attributed to the reaction between CaO and  $\text{CO}_2$  from the atmosphere. In the FTIR spectrum of HAp coating (Figure 2), the wide band at  $3170\text{ cm}^{-1}$  is attributed to the OH stretching of  $\text{H}_2\text{O}$  molecules. The band at cca.  $1650\text{ cm}^{-1}$  is from water (bending modes). The observed functional groups and their corresponding assignments are presented in Table 1.

## 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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