PROTECTION EFFICIENCY OF A NEW COMPLEX HYBRID COATING ON Ti, HAVING TITANIA NANOTUBES, CARBON NANOTUBES AND HYDROXYAPATITE

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In the present paper a hybrid complex coating on Ti, having titania nanotubes, carbon nanotubes (MWCNT) and hydroxyapatite (HA) has been fabricated and characterized. Electrochemical stability was determined in simulated body solution using open circuit technique (OCP) and potentiodynamic polarization plot. Based on electrochemical parameters the porosity and coating efficiency have been computed. The data confirm morpfology aspects from scaning electronic microscopy (SEM) measurements and recommend such coating for protection of Ti implant material.

Keywords: hybrid, titanium, nanotubes, hydroxyapatite, SEM

1. Introduction

The most used metallic implant materials, which are important to be mentioned are CoCr Mo alloys [1], Ti [2], and Ti alloys [3]. All of them have merits [4,5] and demerits [6] in exploitation and, as examples, we have to point out ion release in evironment for CoCrMo alloys and a need to improve mechanical properties for Ti. In order to reduce the disadvantages in their service life, especially for long term, various procedures of surface modifications are performed [7,8]. As an effective procedure, bioinspired coatings with components that mimik natural components such as hydroxiapatite (HA) were the choice in various complex nanoarhitectures. Bioinspired coatings have been elaborated in the last decades using many techniques and a large number of them are sophisticate and expensive [9, 10]. Electrodeposition is one of the cheapest procedures and became more used recently [11]. One of the recent new complexes with elctrodeposited hydroxyapatite proposed in literature [12], was the one with titania and carbon nanotubes (CNT). The enhancement of coating performance is usually expressed in terms of stability and improvement of mechanical properties,

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reducing ion release, and obtaining a more friendly cell response. A quantified value of electrochemical stability increase is protection efficiency of coating in a specific environment and this is the aim of the present paper. The mechanical properties and cell response were presented in a previous paper [12].

2. Experimental Part

2.1. Materials and methods

The titanium samples have the composition as following: 0.002% C, 6.01% Al, 3.95% Zr, 0.16% Fe, 0.004% N, 0.05% Ta, 0.185% O and Ti rest. Multiwall carbon nanotubes (MWCNTs) were purchased from DropSens having more than 90% carbon basis and D x L 10-15 nm x 0.1-10 μm, produced by Catalytic Chemical Vapor Deposition (CCVD).). Oxidation was performed using a mixture of 98% sulfuric acid.

Electrodeposition of MWCNT-COOH/HA on TiO_2 nanotubes complex deposited on titanium plates was performed from an aqueous suspension containing 2 g/L MWCNT-COOH, 9.91 g/L $Ca(NO_3)_2x4H_2O$ and 2.875 g/L $NH_4H_2PO_4$. The deposition was presented with its steps in a previous work [12].

The microstructure characterization of the reference uncoated material and hybrid complex ceramic coating was studied by scanning electronic microscopy (SEM) using the Microscope FEI/Philips XL30 ESEM.

Electrochemical measurements for reference, uncoated Ti and for coated Ti sample were carried out using a Voltalab Potentiostat/ Galvanostat PGZ 301 equipped with Volta Master Sofware. The system used for electrochemical tests was a three-electrode cell with a reference electrode Ag/AgCl (3M), working electrode as Ti coated and uncoated samples and Pt as a counter electrode. The exposed area of the samples to electrolyte test solution which is SBF was 1 cm^2. The SBF composition is the subject of Table 1. All the reagents were purchased from Merck, Germany.

Table 1

SBF chemical composition

NaCl	KCl	$CaCl_2$	$NaHCO_3$	Na_2HPO_2 $2H_2O$	$MgCl_26H_2O$	KH_2PO_4	$MgSO_47H_2O$	glucose
8g/L	0.4g/L	0.18g/L	0.35g/L	0.48g/L	0.10g/L	0.06g/L	0.10g/L	1g/L

The open circuit potential (OCP) versus time and potentiodynamic polarization plot for uncoated Ti and for coated Ti sample in SBF solution were studied. Potentiodynamic polarization tests were carried out at a scan rate of 0.2mV/s from -0.5V versus open circuit potential (OCP) to 3.5V.

The electrochemical procedure for stability evaluation used Tafel slopes, and the electrochemical data permitted to compute porosity (P) and coating efficiency [13] according to the relation (1):

$$P=\frac{R_p}{R_p^0}\times 10^{-\left(\frac{\Delta E_{cor}}{\beta_a}\right)} \quad (1)$$

Porosity (P) is expressed according to Matthes equation where P is the total coating porosity, R_p the polarization resistance of the substrate, R_p^0 the polarization resistance of the coating Ti, ΔE_{cor} is the difference of corrosion potentials between the coating and the substrate, and β_a the anodic Tafel slope of the substrate.

In the formula of coating efficiency:

$$E= 100\ x\ (1- i_{cor}/ i^o_{cor}) \quad (2)$$

where i_{cor} and i^o_{cor} represent as well current density for bioinspired coating sample and for the uncoated Ti.

The samples were tested in terms of bioactivity as well [14]. The ability of samples to induce apatite films on their surface was investigated by immersion in SBF solution for 2 weeks. The samples were suspended in a polyethylene jar and after 2 weeks there were taken out, washed with distilled water and dried at room temperature and their surface were investigated by SEM.

3. Results and discussion

Fig. 1 presents the schematic process of hybrid coating deposition.

The first stage is obtaining TiO_2 nanotubes followed by second step, electrodeposition of MWCNT-COOH which attaches oxygen-containing groups of TiO_2. Following this step, plate-like and needle-like nano-hydroxyapatite films can be electrodeposited, thus forming a TiO_2-MWCNT-COOH-HA composite.

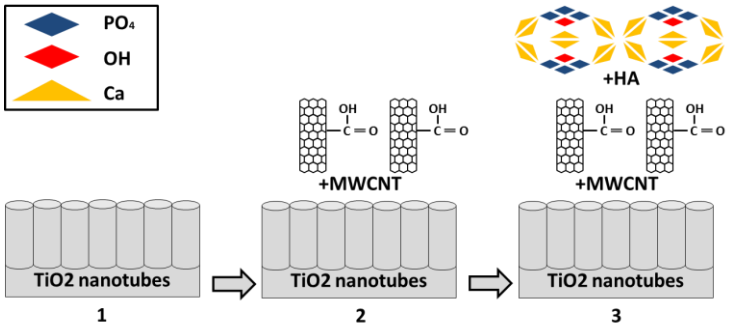


Fig. 1. Schematic process of hybrid coating deposition

In Fig. 2 the morphology from SEM images of bioinspired complex coating (a) is presented in comparison with uncoated Ti sample (b).

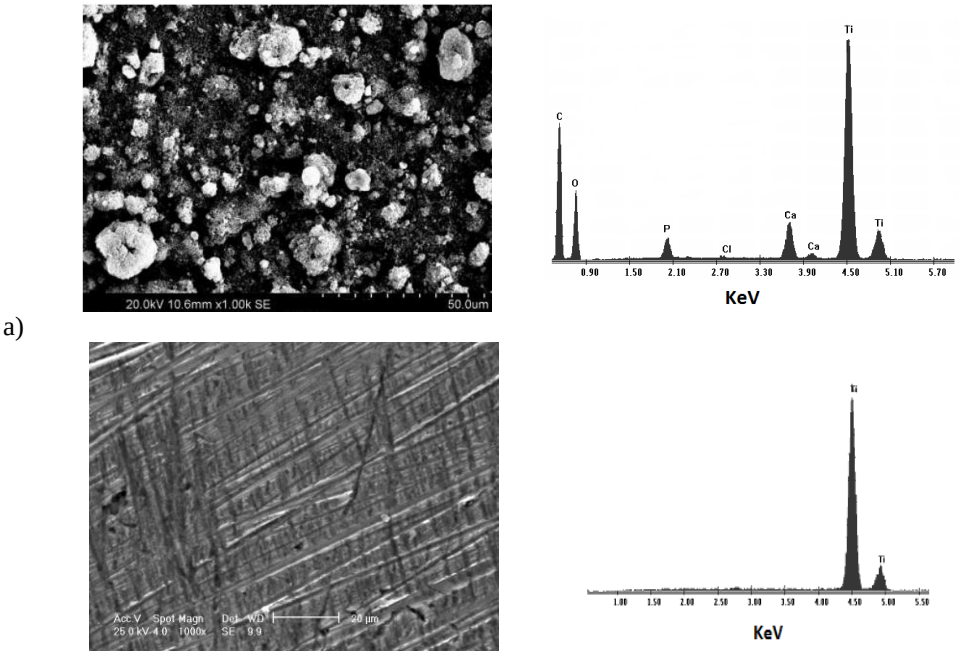


Fig. 2. SEM and EDS of bioinspired complex coating (a) and uncoated Ti sample (b)

Fig. 2a shows that the surface of the sample is porous and indicates that the incorporation of MWCNT-COOH into HA with some agglomeration of HA/MWCNT, resulted in an increased roughness of hybrid material deposited onto Ti substrate. According to the literature data [15] for the potential application of HA/CNT coating in the biomedical field, the rough surface can provide sites for cell attachment. The oxidized MWCNTs are approximately uniformly incorporated in the HA matrix. Similar observation was obtained by C. Lin [16] using electrophoretic deposition of HA-CNT. This image having areas which appear darker shows significantly more porosity than the native oxide layer of Fig. 2b. The dimension of micro pores was around of 0.5µm. EDS of the coated sample detected the presence of P on the alloy surface, incorporated in phosphate groups.

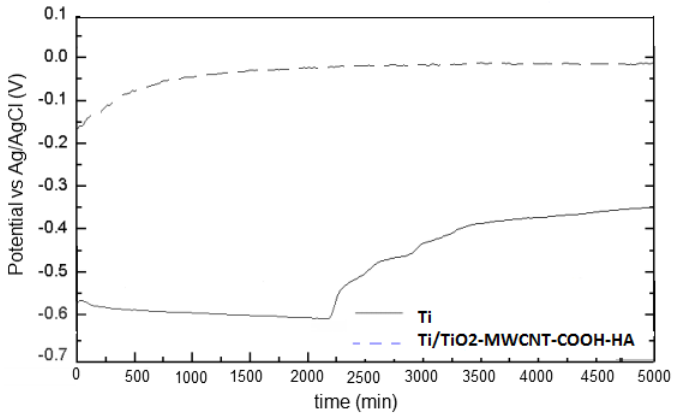


Fig. 3. Variation of OCP in time

Fig. 3 shows the variation of OCP in time. The initial OCP of untreated Ti samples was -0.56 V and then it gradually decreased to -0.605 V (after 2200 min), and finally increase to stable value of -0.38 V due to the dissolution and formation of oxide film on the metal surface. Initial OCP of titanium coated samples is -0.158 V, much higher that uncoated Ti. The OCP of coated samples shifted in the noble direction compared with uncoated samples, showing higher thermodynamic stability. After 5000 minutes the OCP of coated samples was -0.1 V.
In the Fig. 4, potentiodynamic polarization plots of the uncoated and coated Ti are presented and based on this representation, electrochemical parameters are computed and listed in table 2.

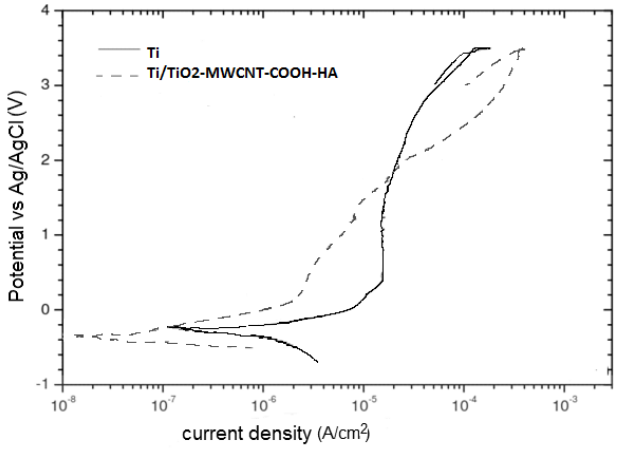


Fig. 4. Polarization plots of uncoated and coated Ti

From Fig. 4, no specimens exhibit appreciable hysteresis loop, indicating the absence of breakdown. This observation is supported by the absence of signs

of pitting on surfaces after polarization tests. At potential below 2.1V there is some improvement in corrosion resistance, the anodic current density of coated samples being lower than that uncoated Ti.

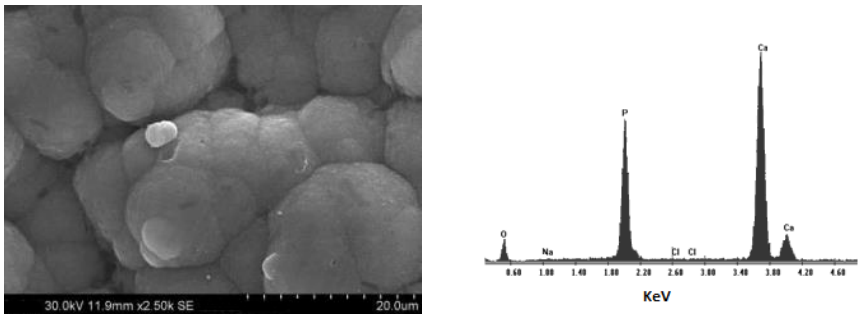
Table 2

Electrochemical parameters of coated and uncoated samples

Samples	E_{cor} (mV)	β_a (mV)	β_c (mV)	i_{cor} ($\mu A/cm^2$)	i_{pas} ($\mu A/cm^2$)	R_p ($K\Omega\ cm^2$)	P (%)	E (%)
Ti	-286	122.3	-294.7	6.012	15.6	10.8	-	
Ti/TiO_2MWCNT-COOH-HA	-302	198.6	-285.5	0.0603	2.94	1076.77	1.351	81, 15

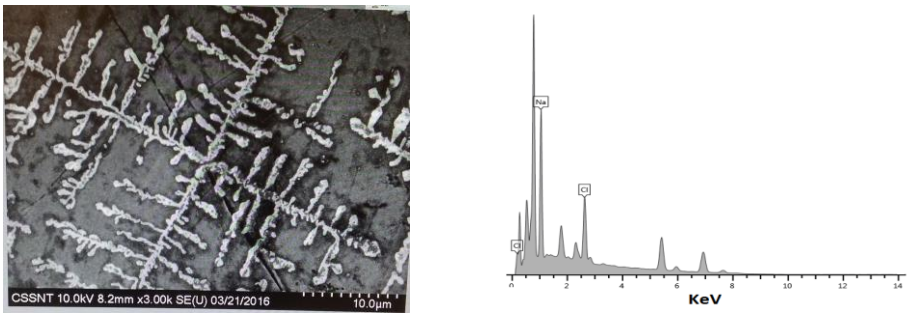
According to Table 2, the coating reduces electrochemical attack, acting as a barrier to prevent interaction of solution and the substrate. The i_{cor} is direct proportional to corrosion rate of materials. For the coated sample, the corrosion current is almost by two orders of magnitude smaller than for uncoated Ti samples. Also, the coated specimens exhibit better passivity performance than uncoated samples by comparing their $i_{pas.}$ The process takes place under cathodic control according to value of cathodic (β_c) and anodic slope (β_a).

After immersion in SBF solution for 2 weeks, apatite was formed only on the coated surface. In Fig. 5a we can see on the surface of the sample some HA spheres. On contrary, NaCl crystals were detected on uncoated Ti samples in fig 5b with a very specific structure.



a)

Fig. 5 a). SEM and EDS for coated sample (a) and for uncoated sample



b)

Fig. 5 b). SEM and EDS for coated sample (b) after two weeks of immersion in SBF

The morphology of the apatite crystals formed on coted titanium after 2 weeks in SBF was similar with to the apatite crystals observed by Guo et al. by microwave irradiation [17].

4. Conclusions

A TiO_2-MWCNT-COOH-HA hybrid composite coating was fabricated on the Ti substrate by electrodeposition method. Ti coated samples present an improvement in corrosion resistance supported by a noble shift of open circuit potential and a lower corrosion current density. SEM and EDS data support electrochemical results and the protection efficency of the hybrid complex coating is 81.15. After 2 weeks immersion in SBF solution, apatite was formed on the coated surface, indicating a good bioactivity.

R E F E R E N C E S

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