CORROSION PROPERTIES OF Ca-DOPED TiO_2 COATINGS

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Abstract

The paper presents the preparation and characterization of TiO_2 coating doped with Ca produced by the sol-gel method using titanium alkoxide as the precursor of titania as well as calcium nitrate as dopant source. These coatings were used to modify the biomedical alloy M30NW. Using the optical microscopy and the atomic force microscopy the topography of synthesized coatings was characterized. Whereas using electrochemical methods the corrosion measurements were carried out. Anticorrosion properties of calcium-doped TiO_2 coating were determined in PBS solution on the basis of corrosion potential Ecor, polarization resistance Rp, corrosion rate CR, current density in the passive range i0.5 and also breakdown Eb and repassivation Erep potentials. Analogous corrosion tests were also made for the uncoated alloy as well as for alloy coated with pure TiO_2 coating.

It was stated that modification of M30NW alloy surface by calcium-doped TiO_2 coating shows anticorrosion properties in PBS solution. These properties are slightly lower compared to a pure TiO_2 coating. The analysis of the topography of TiO_2-based coatings showed that calcium doping increases the surface development and roughness of the obtained coatings.

***Keywords**: biomaterial, surface modification, sol-gel method, doping, corrosion*

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Introduction

Ceramic materials: carbides, nitrides, borides, silicides and oxides are often used to modify the surface of metallic biomaterials to improve their mechanical properties and corrosion. Very good results are achieved through the use of titanium dioxide (TiO_2), which increases the resistance to high temperatures, wear and corrosion of metals and alloys [1-3]. Increased corrosion resistance amounts to increasing the biocompatibility of biomaterials.

An important feature of biomaterials is their bioactivity. The formation of biologically active apatite, whose structure is similar to that of the human bone, is decisive for the integration between the implant and the bone (osseointegration). Studies carried out on titanium implants have shown that the process of spontaneous formation of the apatite layer can be accelerated by modifying the surface of titanium, for example by implanting calcium ions into its surface [4]. In a similar way it is possible to increase the bioactivity of the titanium dioxide layers applied to modify the steel implants [5]. Such modification can be carried out by various methods. In this study, a sol-gel method was used, both as coating and modification method. It shows many advantages compared to other commonly used coating methods: very good control of stoichiometry, homogeneity, purity and chemistry of produced coatings.

The main objective of this study was to determine the effect of calcium ions doping on anticorrosion properties of titanium dioxide coating obtained by the sol-gel method on surface of biomedical alloy M30NW. Corrosion measurements were carried out in PBS solution. Anticorrosion properties of TiO_2 and Ca/TiO_2 coatings were specified based on the determined values of corrosion potential E_{cor}, polarization resistance Rp, corrosion rate CR, current density in passive range i0.5 and also breakdown E_b and repassivation E_{rep} potentials.

Materials and methods

The single-layer titanium dioxide coatings were applied on the surface of biomedical alloy M30NW (AUBERT & DUVAL, France) by the sol-gel method using the dip-coating technique. The samples of alloy, which meets the requirements of ISO 5832-9 standard [6], had the shape of discs with a diameter of 22 mm and a thickness of about 3 mm. Prior to modification alloy samples were ground and polished according to the procedure described in [7]. For pure and calcium-doped TiO_2 coatings titanium tetraisopropoxide was used as the precursor, hydrochloric acid as catalyst, 2-propanol as solvent, and calcium nitrate (1.33 mol/l) as dopant source. The amount of added calcium nitrate solution was chosen so that the molar ratio of Ti/Ca was 20. The composition of sols used for TiO_2 coatings are summarized in TABLE 1.

TABLE 1. The chemical composition of sols with a molar ratio of the reagents.

	Precursor	Solvent	Catalyst	Additive
TiO_2				
	$Ti[OCH_2(CH_3)_2]_4$	C_3H_8O	$HCl_{stęż}$	H_2O
V [ml]	1.256	16.92	0.18	0.1597
Molar ratio	1	52	0.5	2
Ca/TiO_2				
	$Ti[OCH_2(CH_3)_2]_4$	C_3H_8O	$HCl_{stęż}$	$Ca(NO_3)_2$
V [ml]	1.256	16.92	0.18	0.1597
Molar ratio	1	52	0.5	0.05

In the final step, TiO_2 and Ca/TiO_2 coatings was subjected to a heat treatment at temperature of 400°C for 1 hour.

Microscopic analysis of surface of obtained TiO_2 and Ca/TiO_2 coatings was carried out using a metallographic microscope MMT800BT (Mikrolab) and atomic force microscope Dimension Icon (Bruker).

Corrosion measurements were carried out in deoxygenated PBS (Phosphate Buffered Saline) solution with a pH 7.4 and temperature of 37°C, that simulates the human body fluid environment. A potentiostat - galvanostat PGSTAT 30 (Autolab) were used for the measurements. With the use of electrochemical measurement techniques following corrosion parameters were calculated: corrosion potential, polarization resistance, corrosion rate, breakdown potential, repassivation potential, passive current density. All potentials reported in this paper are given versus calomel electrode (E°=0.236 VSHE). Working area of each sample was ca. 0.64 cm^2.

Results and discussions

The TiO_2 coatings obtained showed a very good adhesion to the substrate of biomedical alloy M30NW. There were no cracks or delamination of coatings. Titanium dioxide coating had a golden color and had a thickness of ca. 30 nm regardless of the doping.

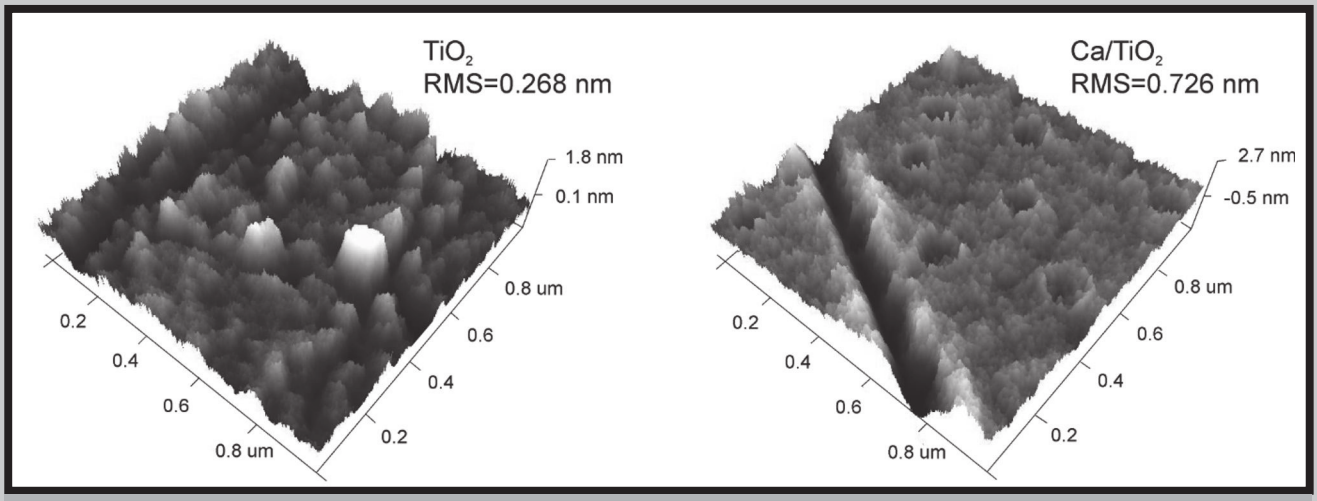

FIG. 1. AFM 3D images of TiO_2 and Ca/TiO_2 coatings.

It was found that doping of calcium ions increases the surface development and roughness of the obtained TiO_2 coatings (FIG. 1). RMS determined from AFM measurements for the undoped coating is 0.26 nm while doping of Ca^{2+} increases its value to 0.726 nm. Differences in RMS are due to the spherical cavities with a diameter of ca. 100 nm and a depth of 2 nm visible on the surface of Ca/TiO_2 coating (FIG. 2).

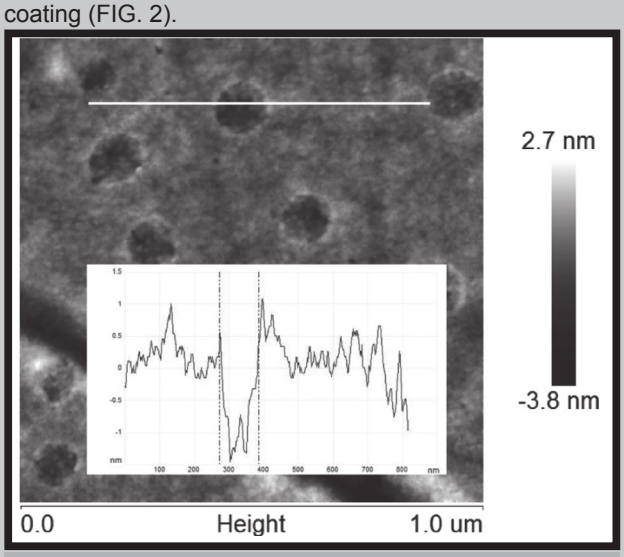

FIG. 2. AFM 2D image and cross section of Ca/TiO_2 coating.

TABLE 2 presents the values of parameters characterizing the corrosive properties of the investigated alloy M30NW both uncoated and coated with TiO_2 coatings: corrosion potential E_{cor}, polarization resistance R_p and corrosion rate CR. The values of corrosion rate were calculated based on determined values of Rp, according to the assumptions of standard ASTM G 102–89 [8], that the corrosion processes at Ecor potential occurs as uniform corrosion.

TABLE 2. Values of corrosion parameters of M30NW alloy in PBS solution.

coating	E_{cor} (V)	R_p (Mohm cm^2)	CR (mm/yr)	p (%)
uncoated	-0.117±0.011	3.4±0.5	(6.1±0.9)×10^{-5}	-
TiO_2	0.213±0.019	39.6±6.3	(5.3±0.8)×10^{-6}	8.8±1.3
Ca/TiO_2	0.232±0.026	26.2±8.4	(8.5±2.5)×10^{-6}	14.1±4.2

Surface modification of M30NW by TiO_2 coating significantly improves its corrosion resistance in PBS solution - coated alloy shows higher values of corrosion potential and polarization resistance, as well as ca. 10-times lower values of corrosion rate. Whereas the calcium ions doping procedure causes a slight deterioration in anticorrosion properties of TiO_2 coating - in case of Ca/TiO_2 - coated alloy the corrosion rate is higher compared to pure TiO_2 - coated alloy.

Results of electrochemical measurements were also used to determine the porosity of the coatings, which is calculated as a ratio of Rp for uncoated alloy and Rp for coated alloy, and it is expressed in percentage. Calcium doping of TiO_2 coatings increases the thus calculated porosity from ca. 9% to ca. 14% (TABLE 2), which in case of biomaterials is advantageous and desirable effect, because higher porosity of the surface promotes osseointegration.

Surface modification of M30NW alloy by TiO_2 coating results in a significant change in the shape and position of the potentiodynamic characteristics in wide range of anodic polarization recorded in PBS solution. Based on potentiodynamic characteristics gathered in wide range of anodic polarization (FIG. 3) following quantities were determined: current density in the passive range (at arbitrary chosen potential E=0.5V) i0.5, breakdown potential E_b and repassivation potential E_{rep}. The values of these quantities are collected in TABLE 3.

In the case of alloy samples coated with TiO_2 the current density in the passive range at a potential equal to E=0.5V is about 3 orders of magnitude lower than for the uncoated alloy.

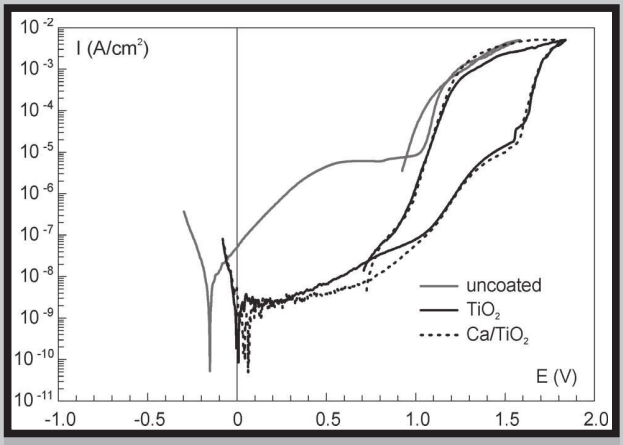

FIG. 3. Potentiodynamic characteristics in anodic range of polarization (scan rate of 1 mV/s).

TABLE 3. Values of corrosion quantities determined from potentiodynamic characteristics.

coating	$i_{0.5}$ (A/cm^2)	E_b (V)	E_{rep} (V)
uncoated	(4.3 ± 0.4) x 10^{-6}	1.047 ± 0.006	0.948 ± 0.001
TiO_2	(6.7 ± 1.1) x 10^{-9}	1.585 ± 0.067	0.759 ± 0.053
Ca/TiO_2	(3.4 ± 1.0) x 10^{-9}	1.598 ± 0.013	0.732 ± 0.001

Also, the breakdown potential values are significantly shifted toward the anodic direction, which confirms the protective properties of titanium dioxide coatings against pitting corrosion. These properties remain unchanged also after doping with calcium ions. Furthermore, for Ca-doped TiO_2 coating the average value of current density read at a potential of 0.5V is even lower, which is a beneficial effect.

Conclusions

Sol-gel method allows to obtain homogeneous coating of titanium dioxide from organic precursor. It is also possible to modify the synthesized sol-gel coating by calcium ion doping using calcium nitrate solution. The doping does not affect the thickness of the coating, but it affects the surface development and roughness of the coating. Synthesized TiO_2-based coatings exhibit anticorrosion properties in PBS solution both at corrosion potential as well as during the anodic polarization. The studies carried out at corrosion potential show that coatings containing calcium ions have a slightly weaker anticorrosive properties compared to pure TiO_2 coatings. Whereas no significant effect of doping were stated during anodic polarization.

Acknowledgements

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STEM CELLS AND THEIR DERIVATIVES – HOPES AND CHALLENGES IN REGENERATIVE MEDICINE

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Abstract

Major goals of contemporary regenerative medicine focus on improvement of irreversible damage of multiple organs and tissues by employing several approaches including recent achievements of cell-based therapies and tissue engineering.

Several types of stem cells (SCs) such as bone marrow (BM)- derived mesenchymal stem cells (MSCs), hematopoietic stem cells (HSCs) as well as SCs with multi- and pluripotent characteristics (PSCs) have been postulated as potential source of cells for therapy. Recently, embryonic stem cells (ESCs) and so called induced pluripotent stem cells (iPS cells) representing "genetically induced" SCs with high differentiation potential, have brought great hope to the field of regenerative medicine and clinical applications. When combined with modern accomplishments of tissue engineering including biocompatible carriers and scaffolds, SCs become leading targets for cell -based regenerative applications.

Although the variety of stem/ progenitor cells have been applied in experimental therapies of several organs injuries, there is still no agreement in scientific and clinical world which subpopulation/s of cells would be the most efficient in such treatment. Moreover, multiple obstacles needs to be overcome prior to optimal application of SCs in regeneration including optimization of ex vivo isolation and expansion conditions or limiting vast adverse features of some SC fractions such as teratogenic potential of ESCs and iPS cells.

Recently, stem cell- derived bioactive components such as cellular microvesicles (MVs) are postulated to play important role in mediating SC activity following transplantation. MVs representing bioactive components carrying SC- derived transcripts (mRNA, miRNA), proteins, enzymes and receptors may participate in tissue regeneration via stimulation of endogenous repair mechanism by activating endogenous target cells in damaged organs.

Thus, the newest trends in regenerative medicine would focus not only on combined applications of biocompatible materials with SC subpopulations, but also with their bioactive acellular components including microvesicles. Unquestionably, successful applications of stem/ progenitor cells and their derivatives in regenerative medicine would need to be safe, ethically acceptable and therapeutically efficient. Sources and application protocols for such optimal stem cell therapy are still being optimized and need scientific discussion.

[Engineering of Biomaterials, 128-129, (2014), 102]