INTERNATIONAL CONFERENCE

MEĐUNARODNA KONFERENCIJA

MEETING POINT OF THE SCIENCE AND PRACTICE IN THE FIELDS OF CORROSION, MATERIALS AND ENVIRONMENTAL PROTECTION

STECIŠTE NAUKE I PRAKSE U OBLASTIMA KOROZIJE, ZAŠTITE MATERIJALA I ŽIVOTNE SREDINE

PROCEEDINGS

KNJIGA RADOVA

Under the auspicies of the
MINISTRY OF EDUCATION, SCIENCE AND TECHNOLOGICAL DEVELOPMENT OF THE REPUBLIC OF SERBIA

Pod pokroviteljstvom
MINISTARSTVO PROSVETE, NAUKE I TEHNOLOŠKOG RAZVOJA REPUBLIKE SRBIJE

May 16-19, 2022 : : Divčibare, Serbia

CIP - Каталогизација у публикацији
Народна библиотека Србије, Београд

620.193/.197(082)(0.034.2)
621.793/.795(082)(0.034.2)
667.6(082)(0.034.2)
502/504(082)(0.034.2)
66.017/.018(082)(0.034.2)

INTERNATIONAL Conference YUCORR (23 ; 2022 ; Divčibare)
Meeting point of the science and practice in the fields of corrosion, materials and environmental protection [Elektronski izvor] : proceedings = Stecište nauke i prakse u oblastima korozije, zaštite materijala i životne sredine : knjiga radova / XXIII YuCorr International Conference = XXIII YuCorr [Jugoslovenska korozija] Međunarodna konferencija, May 16-19, 2022, Divčibare, Serbia = [organized by] Serbian Society of Corrosion and Materials Protection ... [et al.]] ; [organizatori Udruženje inženjera Srbije za koroziju i zaštitu materijala ... [et al.] ; [editors, urednici Miroslav Pavlović, Marijana Pantović Pavlović, Miomir Pavlović]. - Beograd : Serbian Society of Corrosion and Materials Protection UISKOZAM : Udruženje inženjera Srbije za koroziju i zaštitu materijala UISKOZAM, 2022 (Beograd : Serbian Society of Corrosion and Materials Protection UISKOZAM : Udruženje inženjera Srbije za koroziju i zaštitu materijala UISKOZAM). - 1 elektronski optički disk (CD-ROM) ; 12 cm
Sistemski zahtevi: Nisu navedeni. - Nasl. sa naslovne strane dokumenta. - Radovi na engl. i srp. jeziku. - Tiraž 200. - Bibliografija uz većinu radova. - Abstracts.
ISBN 978-86-82343-29-5
а) Премази, антикорозиони -- Зборници б) Превлаке, антикорозионе -- Зборници в) Антикорозиона заштита -- Зборници г) Животна средина -- Заштита -- Зборници д) Наука о материјалима -- Зборници
COBISS.SR-ID 68624905

XXIII YUCORR – International Conference | *Međunarodna konferencija*

PUBLISHED AND CD BURNED BY | *IZDAVAČ I NAREZIVANJE CD*
SERBIAN SOCIETY OF CORROSION AND MATERIALS PROTECTION (UISKOZAM)
UDRUŽENJE INŽENJERA SRBIJE ZA KORZIJU I ZAŠTITU MATERIJALA (UISKOZAM),
Kneza Miloša 7a/II, 11000 Beograd, Srbija, tel/fax: +381 11 3230 028, *office@sitzam.org.rs; www.sitzam.org.rs*

FOR PUBLISHER | *ZA IZDAVAČA* *Prof. dr MIOMIR PAVLOVIĆ, predsednik UISKOZAM*

SCIENTIFIC AREA | *OBLAST:* CORROSION AND MATERIALS PROTECTION **|** *KOROZIJA I ZAŠTITA MATERIJALA*

PAGE LAYOUT | *KOMPJUTERSKA OBRADA I SLOG:* *Dr Marijana Pantović Pavlović*

CIRCULATION | *TIRAŽ:* **200** copies **|** *primeraka*
PUBLICATION YEAR | *GODINA IZDANJA:* **2022**
ISBN 978-86-82343-29-5

The optimization of hydrothermally obtained hydroxyapatite deposition process on titanium by novel *in-situ* process

Katarina Đ. Božić[1,2,*], Miroslav M. Pavlović[1,2], Stefan V. Panić[1], Đorđe N. Veljović[3], Marijana R. Pantović Pavlović[1,2]

[1] *Institute of Chemistry, Technology and Metallurgy, National Institute of the Republic of Serbia, Department of Electrochemistry, University of Belgrade, Njegoševa 12, Belgrade, Serbia*

[2] *Centre of Excellence in Environmental Chemistry and Engineering - ICTM, University of Belgrade, Njegoševa 12, Belgrade, Serbia*

[3] *Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, Belgrade, Serbia*

[*] *katarina.bozic@ihtm.bg.ac.rs*

Abstract

Titanium and its alloys are widely used in medical devices, orthopedic implants, dental implants, and device components of aerospace industries. It is attractive for having superior room and elevated temperature mechanical properties, corrosion resistance, fatigue resistance and low weight. However, titanium and its alloys are not fully applicable replacement in biomedical application. Suitable surface modification of titanium is needed in order to obtain Ti with improved properties. This paper deals with the optimization of the in-situ *anodizing/anaphoretic electrodeposition process of hydrothermally synthesized hydroxyapatite (HAp) on Ti substrate for subsequent obtaining of HAp/TiO_2 composite coatings without multi-stage pre-treatment and post-treatment of titanium and oxidized titanium surface. Coatings were prepared at constant voltage of 60 V and deposition time of 1 min. The morphology of coatings was investigated using optical microscope and field emission scanning electron microscope. Fourier transform infrared spectroscopy measurements were also performed. The coating with optimal properties was obtained by deposition from suspension containing 1.0 M NaOH.*

Keywords: *titanium anodization; in-situ anaphoretic deposition; hydroxyapatite coating; titanium oxide;*

Introduction

Titanium (Ti) and its alloys are one of the leading group of metallic materials used in the biomedical industry, and they are widely used for dental and orthopedic implants. The reason for the increasing use of Ti-based materials in the biomedical field is due to their mechanical properties, good biocompatibility, non-toxicity, high corrosion resistance and low Young's modulus [1,2]. However, the main disadvantages of these materials as implants are their low bioactivity (weak bone-Ti integration) and potential bacterial infections in patients after implantation. Therefore, various methods of modifying the Ti surface have been developed. One of the most commonly used methods is the application of calcium phosphate based coatings, namely hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HAp), on the Ti surface [3].

HAp is a calcium phosphate mineral. It has important role in biomedical practice due to its chemical and mechanical similarities to the mineral component of hard tissues in the human body (bones and cartlages). In addition, HAp owns good bioactivity, biodegradability and osteoconductivity. Owing to these properties and similarity with the chemical composition of human bone, it is often used in prosthetic applications [4].

However, HAp has poor mechanical properties; therefore, HAp is deposited on Ti-based implants to achieve both bioactivity and mechanical resistance. Various methods are used to deposit HAp on a Ti-based substrate, such as electrophoretic deposition, plasma spraying, and the sol-gel process [5].

Electrophoretic deposition (EPD) is a widely used technique for the deposition of various biomaterials. The EPD process takes place in two phases. In the first phase, positive or negative charges are generated on the suspended particles; the suspension is stabilized; the second phase involves the deposition of the charged species on the surface of the oppositely charged electrodes. Electrophoretic deposition can be cathodic and anodic [6].
The goal of this study was optimization of novel *in-situ* anodizing/anaphoretic electrodeposition process of hydrothermally obtained HAp on the Ti substrate in order to obtain HAp/TiO_2 composite coatings [7].

Materials and methods

HAp powder was synthesized by the modified hydrothermal method described in the literature [8-9] as follows: the initial solution was obtained by dissolving the appropriate amount of $Ca(NO_3)_2 \cdot 4H_2O$, $Na_2H_2EDTA \cdot 2H_2O$, $NaH_2PO_4 \cdot 2H_2O$ and urea in 1.5 dm^3 of deionized water. All chemicals were *p.a.* grade from Acros Organics. The Ca/P ratio value for starting solution was 1.67 (stoichiometric ratio of HAp). After dissolving all the chemicals, the flask with the solution was transferred to an autoclave and thermally treated at 160 ºC under 8 bar for 3 h. After cooling, the obtained precipitate was collected by vacuum filtration, washed with deionized water, and dried at 105 ºC.
The deposition of the coatings HAp/TiO_2 was performed by a new *in-situ* method of anodizing/anaphoretic electrodeposition developed by Pantović Pavlović et al. [7]. For deposition of coatings, the starting HAp suspension was prepared by dissolving 1.0 g of hydrothermally obtained HAp powder in 50 vol.% of absolute ethanol and 50 vol.% of 0.1 M NaOH (total volume = 100 mL). NaOH was further added in the suspension to obtain 0.1, 0.5, 1.0 and 1.2 M NaOH suspensions of HAp in ethanol. The suspensions were prepared by adding an appropriate amount of dry NaOH. Ti plates (20 mm × 10 mm × 0.89 mm, Alfa Aesar, 99.7% purity, grade 2 Ti) were used as substrates for the deposition of HAp/TiO_2 coatings. First, Ti plates are prepared by grinding with silicon carbide sandpaper (SiC) of grades from 600 to 3000. After that, the substrates were mechanically polished with micropolish alumina pastes of 0.3 and 0.05 µm, respectively. The anode was a Ti plate prepared as described, while a pair of stainless-steel plates 1Cr18Ni9Ti were used as the cathode. The anodization was performed under 60 V because the roughest substrate was obtained [10]. The CPX400DP potentiostat/galvanostat from Aim and Thurlby Thandar Instruments was used as the power source. All suspensions were stirred for 2 hours before and during the electrodeposition process using a magnetic stirrer. The deposition time for all HAp/TiO_2 coatings was 1 min in a potentiostatic regime.
Optical images of the synthesized HAp/TiO_2 coatings were recorded by Olympus CX41 optical microscope. A field-emission scanning electron microscope (FE-SEM) Tescan Mira 3 XMU FEG-SEM was used to analyze the morphology of the obtained coatings. Fourier transform infrared spectroscopy (FTIR) was carried out using a Michelson MB Series Bomen FTIR spectroscope (Hartmann Braun) to detect the bond types in the material.

Results and discussion

Figure 1 shows optical images of HAp/TiO_2 coatings on Ti substrate obtained at different NaOH concentrations in suspensions. At the lowest NaOH concentrations, the anodization of substrate surface was occurred, which could be seen as the yellow color of the substrate. This can be explained by the insufficient concentration of OH^- ions that would surround the HAp particles. The OH^- ion was insufficient to maintain stable suspension and as a consequence, all the applied voltage was spent on surface anodization process. At the surface of the coating obtained from a suspension containing 0.5 M NaOH, the beginning of the formation of the HAp layer is visible in addition to the yellow color of the substrate and anodized layer.

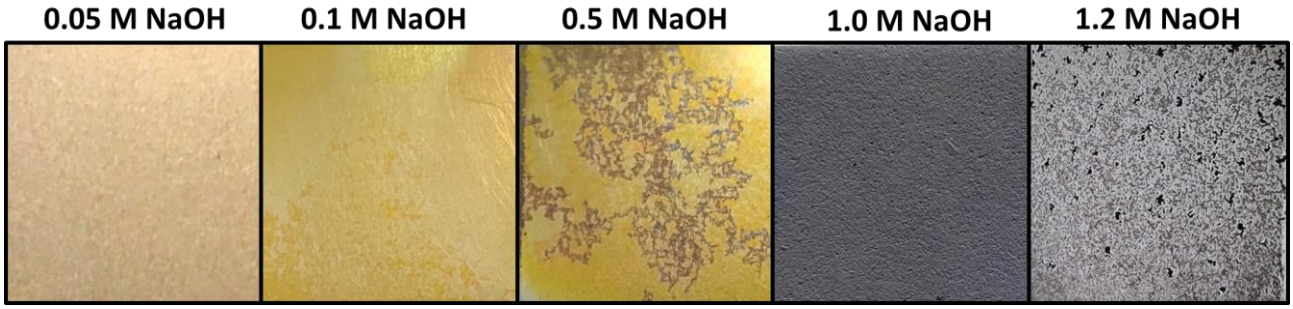

Figure 1. *Optical images of HAp/TiO_2 coatings on Ti substrate produced from suspensions of hydrothermally obtained HAp powder + NaOH*

As it can be seen from Figure 1, the best results were obtained with NaOH concentration of 1.0 M, where the resulting coating is uniform, firm and it covers the whole surface. On the other hand, for 1.2 M NaOH, formation of holes in the coating is visible due to the evolution of gas, which leads to a conclusion that the process is too tempestuous for the given experimental set-up.
Figure 2 shows FE-SEM images of HAp/TiO_2 composite coatings obtained from suspensions containing 1.0 M NaOH and 1.2 M NaOH. As it can be seen from Figure 2, a coating consisting of relatively uniform spherical agglomerates, having several microns in the size, but considerably more uniform coating was obtained from the 1.0 M NaOH suspension. Bright spots are visible in the Figure 2 showing HAp powder obtained from the 1.2 M NaOH suspension, which indicates that the holes were formed in the coating due to the release of gas.

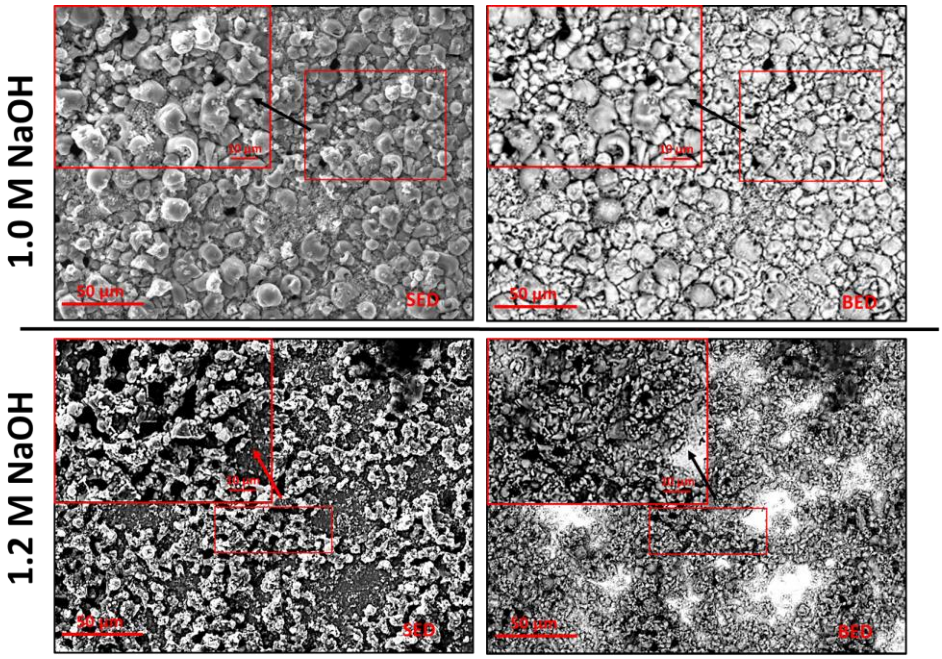

Figure 2. *FE-SEM images of HAp/TiO_2 coatings on Ti substrate produced from suspensions of hydrothermally obtained HAp powder and NaOH*

FTIR spectra of HAp powder and synthesized HAp/TiO_2 coating are shown in Figure 3. These spectra confirm the presence of functional groups related to HAp.

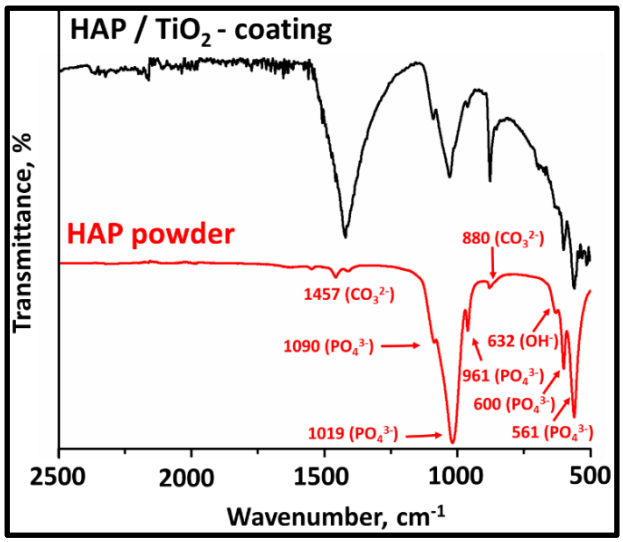

Figure 3. *FTIR spectrum of hydrothermally obtained HAp powder and HAp/TiO_2 coating on Ti substrate*

The peaks at 561, 600, 961, 1019 and 1090 cm^{-1} are the characteristic bands for PO_4^{3-}. The OH^- characteristic band occurs at 632 cm^{-1}. The bands at wavenumbers 880 and 1457 cm^{-1} come from incorporated CO_3^{2-} in the HAp structure [11]. These CO_3^{2-} peaks originate from CO_2 that was absorbed from the air. HAp is well known to easily substitute OH^- by CO_3^{2-}.

Conclusions

The presented study investigated the optimization of the *in-situ* anodizing/anaphoretic electrodeposition process of hydrothermally obtained HAp on Ti substrate in order to obtain HAp/TiO_2 composite coatings. The formation of these coatings was confirmed by optical microscope, FE-SEM and FTIR. The best results were obtained by applying of 60 V, from the solution containing 1.0 M NaOH. The coating showed uniformity, firmness and excellent coverage of the entire surface. Holes appeared in the coating obtained from 1.2 M NaOH suspension due to gas evolution. Further investigation under lower current in potentiostatic regime should be further investigated.

Acknowledgements

This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grant No. 451-03-68/2022-14/200026).

References

1. J. Li, P. Zhou, S. Attarilar, H. Shi, Innovative Surface Modification Procedures to Achieve Micro/Nano-Graded Ti-Based Biomedical Alloys and Implants, *Coatings*, **11(6)**, 647, 2021.
2. M. Avci, B. Yilmaz, A. Tezcaner, Z. Evis, Strontium doped hydroxyapatite biomimetic coatings on Ti6Al4V plates, *Ceram. Int.*, **43(12)**, 9431–9436, 2017.
3. X. Zhang *et al.*, Novel ternary vancomycin/strontium doped hydroxyapatite/graphene oxide bioactive composite coatings electrodeposited on titanium substrate for orthopedic applications, *Colloids Surfaces A Physicochem. Eng. Asp.*, **603**, 2020.
4. V. Saxena, I. Shukla, L. M. Pandey, "Hydroxyapatite: An inorganic ceramic for biomedical applications," in *Materials for Biomedical Engineering: Nanobiomaterials in Tissue Engineering*, A.-M. Holban and A. M. Grumezescu, Eds. Elsevier, 2019, 205–249.
5. L. M. Muresan, "Corrosion Protective Coatings for Ti and Ti Alloys Used for Biomedical Implants," in *Intelligent Coatings for Corrosion Control*, A. Tiwari, J. Rawlins, and L. H.

Hihara, Eds. Boston: Elsevier Inc., 2015, 585–602.
6. S. A. Batool, A. Wadood, S. W. Hussain, M. Yasir, M. A. Ur Rehman, A Brief Insight to the Electrophoretic Deposition of PEEK-, Chitosan-, Gelatin-, and Zein-Based Composite Coatings for Biomedical Applications: Recent Developments and Challenges, *Surfaces*, **4**(**3**), 205–239, 2021.
7. M. R. Pantović Pavlović, S. G. Eraković, M. M. Pavlović, J. S. Stevanović, V. V. Panić, N. L. Ignjatović, Anaphoretical/oxidative approach to the in-situ synthesis of adherent hydroxyapatite/titanium oxide composite coatings on titanium, *Surf. Coatings Technol.*, **358**, 688–694, 2019.
8. Dj. Veljovic, T. Matic, T. Stamenic, V. Kojic, S. Dimitrijevic-Brankovic, M. J. Lukic, S. Jevtic, Z. Radovanovic, R. Petrovic, D. Janackovic, Mg/Cu co-substituted hydroxyapatite – Biocompatibility, mechanical properties and antimicrobial activity, *Ceram. Int.*, **45**(**17**, **Part A**), 22029–22039, 2019.
9. T. Matić, M. L. Zebić, V. Miletić, I. Cvijović-Alagić, R. Petrović, Dj. Janaćković, Dj. Veljović, Sr,Mg co-doping of calcium hydroxyapatite: Hydrothermal synthesis, processing, characterization and possible application as dentin substitutes, *Ceram. Int.*, **48**(**8**), 11155–11165, 2022.
10. M. R. Pantović Pavlović, M. M. Pavlović, S. Eraković, T. Barudžija, J. S. Stevanović, N. Ignjatović, V. V. Panić, Relationship between the properties of an interlayer formed by in situ Ti anodization and anaphoretically deposited hydroxyapatite, *J. Serbian Chem. Soc.*, **84**(**11**), 1305–1318, 2019.
11. K. Lin, J. Chang, Y. Zhu, W. Wu, G. Cheng, Y. Zeng, M. Ruan, A Facile One-Step Surfactant-Free and Low-Temperature Hydrothermal Method to Prepare Uniform 3D Structured Carbonated Apatite Flowers, *Cryst. Growth Des.*, **9**(**1**), 177–181, 2009.