(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 3 757 257 A1

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
30.12.2020 Bulletin 2020/53

(51) Int Cl.:
C25D 11/02 *(2006.01)* ***C25D 11/26*** *(2006.01)*

(21) Application number: **20460020.9**

(22) Date of filing: **27.04.2020**

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
KH MA MD TN

(30) Priority: **25.06.2019 PL 43037519**

(71) Applicant: **Politechnika Slaska**
44-100 Gliwice (PL)

(72) Inventors:
- **Simka, Wojciech**
  40-748 Katowice (PL)
- **Kazek-Kesik, Alicja**
  41-310 Dabrowa Górnicza (PL)
- **Lesniak, Katarzyna**
  42-400 Zawiercie (PL)

(54) THE FORMATION METHOD OF POROUS ANTIBACTERIAL COATINGS ON TITANIUM AND TITANIUM ALLOYS SURFACE

(57) The method of titanium surface modification by plasma electrochemical oxidation in $Ca(H_2PO_2)_2$ baths at a concentration from 0.01 mol·dm^{-3} to 5 mol·dm^{-3} with an anodic current density from 1 mA·cm^{-2} to 250 mA·cm^{-2} and applied voltage from 50 V to 600 V is characterized by immersing the surface-modified element in an aqueous salt solution with insoluble particles of silver(I) oxide Ag_2O, copper(I) oxide Cu_2O or copper(II) oxide CuO at a concentration from 1 g·dm^{-3} to 400 g·dm^{-3}.

EP 3 757 257 A1

Description

[0001] The subject of this invention is a formation method of the porous oxide layers on the surface of titanium and titanium alloys by plasma electrochemical oxidation. Due to the oxidation in baths containing suspended, insoluble particles of silver and copper compounds, the obtained oxide layers are intended to be characterized by antimicrobial and/or bacteriostatic properties.

[0002] Titanium and titanium alloys are used as long-term implant materials characterized by good biocompatibility with hard and soft tissue of the human body. During the implantation process, there is a risk of human tissues septic inflammation occurrence. Therefore, patients are being treated with bactericides such as antibiotics. However, because of the increasing resistance of bacteria to antibiotics, there are being carried out the studies of the alternative antibacterial agents. A good example of different than antibiotics bactericides can be the modified implant biomaterials containing silver or copper in their composition. So far in the literature, there are known studies of obtaining layers containing silver or copper compounds formed from soluble forms of these elements compounds.

[0003] The patent no. CN 101899700 describes the method of obtaining bioactive coatings on the surface of titanium and magnesium alloys by the plasma electrochemical oxidation using bath consisting of $AgNO_3$, which results in the formation of porous oxide layers containing calcium, phosphorus and silver improving the bioactivity of the coatings, as well as their corrosion resistance and decreasing the risk of bacterial infections caused by the implantation process. The thickness of the coating formed on the surface of the titanium alloy measured 50-85 μm, the porosity of the coating was in the range from 20% to 30%, and the determined adhesion of the coating to the substrate was 23-40 MPa. The patent no. CN 108543109 describes the formation method of composite materials with antibacterial properties. The composite consists of ceramic TiO_2 and silver nanoparticles on the surface of a titanium alloy intended for use as an implant for bone tissue. In the paper "Antibacterial properties of Ag (or Pt)-containing calcium phosphate coatings formed by micro-arc oxidation" (W.H. Song, H.S. Ryu, S.H. Hong, Journal of Biomedical Materials Research Part A, 88 (1) (2009) 246) there is known the method of plasma electrochemical oxidation using the bath containing: 0.04 mol·dm^{-3} $C_3H_7Na_2O_6P \cdot 5H_2O$, 0.40 mol·dm^{-3} $(CH_3COO)_2Ca \cdot H_2O$ and $AgNO_3$ or CH_3COOAg in the concentration range 0.00003-0.004 mol·dm^{-3} at 250-450 V. The manuscript "Antibacterial titanium surfaces for medical implants" (S. Ferraris, S. Spriano, Materials Science and Engineering, 61 (2016) 965) presents the method of plasma electrochemical oxidation using a bath containing 7-25 nm silver nanoparticles, $(CH_3COO)_2Ca$ and calcium glycerophosphate. The paper "Fabrication of oxide layer on zirconium by micro-arc oxidation: Structural and antimicrobial characteristics" (S. Fidan, F. Muhaffel, M. Riool, G. Cempura, L. de Boer, S. A. J Zaat, A. Czyrska- Filemonowicz, H. Cimenoglu, Materials Science and Engineering, 71 (2017) 565) presents the method of plasma electrochemical oxidation using the bath containing Na_2SiO_3, NaOH and CH_3COOAg. In the manuscript "Characteristics of multi-layer coatings synthesized on Ti6Al4V alloy by micro-arc oxidation in silver nitrate added electrolytes" (F. Muhaffel, G. Cempura, M. Menekse, A. Czyrska-Filemonowicz, N. Karaguler, H. Cimenoglu, Surface and Coating Technology. 307 (2016) 308) there is known the method of plasma electrochemical oxidation in the bath containing Na_2HPO_4, $Ca(CH_3COO)_2 \cdot H_2O$ and $AgNO_3$ in concentrations 0.1 g·dm^{-3} or 0.4 g·dm^{-3}. In the manuscript "Corrosion Resistance and Antibacterial Properties of Ag-Containing MAO Coatings on AZ31 Magnesium Alloy Formed by Microarc Oxidation" (S. Ryu, SH Hong, Journal of Electrochemical Society, 157 (2010) 131), the method of plasma electrochemical oxidation in bath containing Na_2SiO_3 and $AgNO_3$ is known. The paper "High-current anodization: A novel strategy to functionalize titanium-based biomaterials" (C. Chang, X. Huang, Y. Liu, L. Bai, X. Yang, R. Hang, B. Tang, PK Chu, Electrochimica Acta, 173 (2015) 345) presents the method of plasma electrochemical oxidation in the bath containing 7.6 g·dm^{-3} Na_3PO_4, 9.4 g·dm^{-3} $Ca(NO_3)_2$ and 1.0 g·dm^{-3} $AgNO_3$. The publication "In vitro antibacterial activity of porous TiO2-Ag composite layers against methicillin-resistant Staphylococcus ureus" (B.S. Necula, L.E. Fratila-Apachitei, S.A. Zaat, I. Apachitei, J. Duszczyk, Acta Biomaterialia, 5 (2009) 3573) presents the method of plasma electrochemical oxidation in the bath containing 0.15 mol·dm^{-3} $Ca(CH_3COO)_2$ or 0.02 mol·dm^{-3} calcium glycerophosphate with the addition of 0.03 g·dm^{-3} of nanoparticles Ag. The manuscript "Characteristics of multi-layer coating formed on commercially pure titanium for biomedical applications" (D. Teker, F. Muhaffel, M. Menekse, NG Karaguler, M. Baydogan, H. Cimenoglu, Materials Science and Engineering C, 48 (2015) 579) presents the method of anodic electrochemical oxidation using the bath containing Na_2HPO_4, $Ca(CH_3COO)_2$ and 0.0025 mol·dm^{-3} CH_3COOAg. In the paper "Corrosion behavior of Zn-incorporated antibacterial TiO2 porous coating on titanium" (X. Zhang, H. Wang, J. Li, X. He, R. Hang, X. Huang, L. Tian, B. Tang, Ceramic International, 32 (2016) 919) there is presented the method of anodic electrochemical oxidation in the bath consisting of 0.02 mol·dm^{-3} sodium β-glycerophosphate, 0.1 mol·dm^{-3} $Ca(CH_3COO)_2$, 0.1 mol·dm^{-3} $Zn(CH_3COO)_2$ and 6 g·dm^{-3} of nanoparticles Ag. In the manuscript "Energy-Dispersive X-Ray Spectroscopy Mapping of Porous Coatings Obtained on Titanium by Plasma Electrolytic Oxidation in a Solution Containing Concentrated Phosphoric Acid with Copper Nitrate" (K. Rokosz, T. Hryniewicz, L. Dudek, A. Schutz, J. Heeg and M. Wienecke, Advances in Materials Science, 16 (2016) 15) there is presented the method of anodic oxidation of titanium using the bath containing Cu(N03)2. 1 dm^3 of bath may contain 85% H_3PO_4 and 600 g of dissolved $Cu(NO_3)_2$. The process can be carried out at 450 V. In the work "Catalytically active cobalt-copper-oxide layers on aluminium and titanium" (I.V. Lukiyanchuk, I.V. Chernykh, V.S. Rudnev, A. Yu Ustinov, L.M. Tyrina, P.M. Nedozorov, E.E. Dmitrieva, Protection of Metals and Physical Chemistry of Surfaces, 50 (2014) 209) there is known the method of obtaining oxide layers on the titanium surface by the plasma electrolytic oxidation treatment, followed by the modification of the obtained oxide layers with copper and cobalt by impregnation in solutions of soluble copper and cobalt salts. The manuscript "Biological Activity and Antibacterial Property of Nano-structured TiO2 Coating Incorporated with Cu Prepared by Micro-arc Oxidation" (W. Zhu, Z. Zhang, B. Gu, J. Sun, L. Zhu, Journal of Materials Science & Technology, 29 (2013) 237) a plasma electrochemical oxidation method is known using the bath containing 0.05 mol·dm^{-3} sodium β-glycerophosphate, 0.1 mol·dm^{-3} $Ca(CH_3COO)_2$ and 0.05 mol·dm^{-3} $(CH_3COO)_2Cu$. The publication "SEM, EDS and XPS Analysis of the Coatings Obtained on Titanium after Plasma Electrolytic Oxidation in Electrolytes Containing Copper Nitrate" (K. Rokosz, T. Hryniewicz, D. Matýsek, S. Raaen, J. Valíček, L. Dudek, M. Harničárová, Materials, 9 (2016) 318) describes the method of anodic oxidation of titanium from the bath containing $Cu(NO_3)_2$. 1 dm^3 of bath may contain 85% H_3PO_4 and 10-600 g of dissolved $Cu(NO_3)_2$. In the paper "Microstructure and antibacterial properties of Cu-doped TiO2 coating on titanium by micro-arc oxidation" (X. Yao, X. Zhang, H. Wu, L. Tian, Y. Ma, B. Tang, Applied Surface Science , 292 (2014) 944) there is known the method of plasma electrochemical oxidation in the bath containing 2 g·dm^{-3} NaOH, 15 g·dm^{-3} NaH_2PO_4 and 3 g·dm^{-3} Cu nanoparticles. In the manuscript "One-step fabrication of cytocompatible micro/nano-textured surface with TiO2 mesoporous arrays on titanium by high current anodization" (X. Huang, Y. Liu, H. Yu, X. Yang, Y. Wang, R. Hang, B. Tang, Electrochimica Acta, 199 (2016) 116) there is known the method of anodic electrochemical oxidation using the bath containing 3.8-7.6 g·dm^{-3} Na_3PO_4 and 1.0-8.0 g·dm^{-3} $Cu(NO_3)_2$. The paper "The dual function of Cu-doped TiO2 coatings on titanium for application in percutaneous implants" (L. Zhang, J. Guo, X. Huang, Y. Zhang, Y. Han, Journal of Materials Chemistry, 4 (2016) 3788) presents the method of anodic electrochemical oxidation using the bath containing 0.02 mol·dm^{-3} sodium β-glycerophosphate, 0.02 mol·dm^{-3} $Ca(CH_3COO)_2$ and 0.00125-0.00500 mol·dm^{-3} $Cu(CH_3COO)_2$. The patents No. PL 225226 and PL 225227 present the method of anodic electrochemical oxidation of tantalum, niobium and zirconium in the suspension of insoluble calcium silicate $CaSiO_3$ at a concentration

of 1-300 g·dm^{-3}. The patent no. PL 396115 present the method of plasma electrochemical oxidation of titanium and its alloys in suspension $ZrSiO_4$ at a concentration of 1-100 g·dm^{-3} with the addition of an alkali metal hydroxide at a concentration of 5-100 g·dm^{-3}, temperature of 15-50°C, anodic current density 5-500 mA·dm^{-2} and applied voltage 1-600 V for 1-30 minutes. In the patent no. PL 214630 there is presented the method of electrochemical plasma oxidation of Ti-xNb-yZr alloys in a $Ca(H_2PO_2)_2$ solution at a concentration of 1-150 g·dm^{-3} or in a NaH_2PO_2 solution at a concentration of 1-250 g·dm^{-3}, temperature in the range of 15-50°C, anodic current density of 5-5000 mA·dm^{-2} and applied voltage of 100-650 V for 1-60 minutes.

[0004] The aim of the invention is to develop a method allowing to obtain the porous oxide layers with incorporated compounds with antibacterial properties.

[0005] The essence of the invention is the surface modification of titanium and titanium alloys via plasma electrochemical oxidation in baths containing $Ca(H_2PO_2)_2$ at a concentration from 0.01 mol·dm^{-3} to 5 mol·dm^{-3}, at the anodic current density from 1 mA·cm^{-2} to 250 mA·cm^{-2} and applied voltage from 50 V to 600 V. The surface-modified elements are immersed in an aqueous salt solution containing insoluble silver(I) oxide Ag_2O, copper(I) oxide Cu_2O or copper(II) oxide CuO at a concentration from 1 to 400 g·dm^{-3}.

[0006] The invention describes the method of the plasma electrochemical oxidation of titanium and its titanium alloys in suspensions containing insoluble silver or copper compounds in the form of the oxides. In this way, it is possible to obtain porous oxide layers incorporated with particles of compounds characterised by the antibacterial properties. The addition of mentioned silver and copper suspension compounds can be a one-step modification of the surface of titanium and its alloys. Thanks to this, there is a chance to eliminate the necessity of high, oral antibiotic delivery route, which is the main cause of increasing bacteria resistance to antibiotics. Additionally, the number of side effects and allergic reactions related to antibiotic treatment can be reduced. The surfaces anodised via plasma electrolytic oxidation process are porous and rough, which promotes the proliferation of living cells and supports the osseointegration process.

Example 1: The titanium implant, pre-treated by polishing, degreasing, etching and rinsing in demineralised water is placed in the solution containing 0.1 mol·dm^{-3} $Ca(H_2PO_2)_2$ and the suspension of 10 g·dm^{-3} Ag_2O. After placing the implant in the anodising bath, the electrolytic plasma oxidation process is carried out by polarizing it with the anodic current density of 150 mA·cm^{-2}. The process is carried out for 5 minutes, with the maximum voltage of 300 V. After the process, the implant is rinsed in demineralised water and air-dried at 45°C.

Example II: The implant made of Ti-13Nb-13Zr alloy, mechanically pre-treated, degreased, etched and rinsed in demineralised water is placed in the anodising bath containing 0.01 mol·dm^{-3} $Ca(H_2PO_2)_2$ and a suspension of 100 g·dm^{-3} Cu_2O. After placing the implant in the bath, the electrolytic plasma oxidation process is carried out by polarizing it with the anodic current density of 100 mA·cm^{-2}. The process is carried out for 7 minutes, with the maximum voltage of 350 V. After the process, the implant is rinsed in demineralised water and air-dried at 45°C.

Example III: The implant made of Ti-15Mo alloy, mechanically pre-treated, degreased, etched and rinsed in demineralised water is placed in the anodising bath containing 5 mol·dm^{-3} $Ca(H_2PO_2)_2$ and the suspension of 200 g·dm^{-3} CuO. After placing the implant in the bath, the electrolytic plasma oxidation process is carried out by polarizing it with the anodic current density of 200 mA·cm^{-2}. The process is carried out for 5 minutes, with the maximum voltage of 400 V. After the process, the implant is rinsed in demineralised water and air-dried at 45°C.

Claims

1. The method of titanium surface modification by plasma electrochemical oxidation in $Ca(H_2PO_2)_2$ baths at the concentration from 0.01 mol·dm^{-3} to 5 mol·dm^{-3} with the anodic current density from 1 mA·cm^{-2} to 250 mA·cm^{-2} and applied voltage from 50 V to 600 V is **characterized by** immersing the surface-modified element in the aqueous salt solution with insoluble particles of silver(I) oxide Ag_2O, copper(I) oxide Cu_2O or copper(II) oxide CuO at a concentration from 1 g·dm^{-3} to 400 g·dm^{-3}.

Europäisches Patentamt
European Patent Office
Office européen des brevets

EUROPEAN SEARCH REPORT

Application Number
EP 20 46 0020

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	KAZEK-KESIK ALICJA ET AL: "Surface characterisation of Ti-15Mo alloy modified by a PEO process in various suspens", MATERIALS SCIENCE AND ENGINEERING C, vol. 39, 12 March 2014 (2014-03-12), pages 259-272, XP029029210, ISSN: 0928-4931, DOI: 10.1016/J.MSEC.2014.03.008 * page 260, right-hand column, paragraph 2 - page 264, left-hand column, paragraph 2 * * page 271, left-hand column, paragraph 3 *	1	INV. C25D11/02 C25D11/26
A,D	NECULA B S ET AL: "In vitro antibacterial activity of porous TiO"2-Ag composite layers against methicillin-resistant Staphylococcus aureus", ACTA BIOMATERIALIA, ELSEVIER, AMSTERDAM, NL, vol. 5, no. 9, 1 November 2009 (2009-11-01), pages 3573-3580, XP026693830, ISSN: 1742-7061, DOI: 10.1016/J.ACTBIO.2009.05.010 [retrieved on 2009-05-18] * page 3574, left-hand column, paragraph 4 - page 3574, right-hand column, paragraph 4 * * page 3575, right-hand column, paragraph 2 - page 3576, right-hand column, last paragraph *	1	TECHNICAL FIELDS SEARCHED (IPC) C25D
A	PL 214 958 B1 (POLITECHNIKA SLASKA IM WINCENT [PL]) 31 October 2013 (2013-10-31) * paragraph [0003] * * paragraphs [0006] - [0015] *	1	

-/--

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	6 October 2020	Crottaz, Olivier

2

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

Europäisches Patentamt
European Patent Office
Office européen des brevets

EUROPEAN SEARCH REPORT

Application Number
EP 20 46 0020

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	DATABASE EPODOC [Online] EUROPEAN PATENT OFFICE, THE HAGUE, NL; 20 May 1996 (1996-05-20), XP002800828, Database accession no. RU-94028190-A * abstract * & RU 94 028 190 A (INST KHIM DAL NEVOSTOCHNOGO OTDEL RAN) 20 May 1996 (1996-05-20) * abstract * -----	1	
A,D	MUHAFFEL FAIZ ET AL: "Characteristics of multi-layer coatings synthesized on Ti6Al4V alloy by micro-arc oxidation in silver nitrate added electrolytes", SURFACE AND COATINGS TECHNOLOGY, ELSEVIER BV, AMSTERDAM, NL, vol. 307, 1 September 2016 (2016-09-01), pages 308-315, XP029823815, ISSN: 0257-8972, DOI: 10.1016/J.SURFCOAT.2016.09.002 * page 308, right-hand column, paragraph 2 - page 310, left-hand column, last paragraph * -----	1	TECHNICAL FIELDS SEARCHED (IPC)
A	CN 102 677 125 A (NW INST NON FERROUS METAL RES) 19 September 2012 (2012-09-19) * abstract * -----	1	

The present search report has been drawn up for all claims

2

Place of search	Date of completion of the search	Examiner
The Hague	6 October 2020	Crottaz, Olivier

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 20 46 0020

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

06-10-2020

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
PL 214958	B1	31-10-2013	NONE	
CN 102677125	A	19-09-2012	NONE	

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- CN 101899700 **[0003]**
- CN 108543109 **[0003]**
- PL 225226 **[0003]**
- PL 225227 **[0003]**
- PL 396115 **[0003]**
- PL 214630 **[0003]**

Non-patent literature cited in the description

- **W.H. SONG ; H.S. RYU ; S.H. HONG.** Antibacterial properties of Ag (or Pt)-containing calcium phosphate coatings formed by micro-arc oxidation. *Journal of Biomedical Materials Research Part A,* 2009, vol. 88 (1), 246 **[0003]**
- **S. FERRARIS ; S. SPRIANO.** Antibacterial titanium surfaces for medical implants. *Materials Science and Engineering,* 2016, vol. 61, 965 **[0003]**
- **S. FIDAN ; F. MUHAFFEL ; M. RIOOL ; G. CEMPURA ; L. DE BOER ; S. A. J ZAAT ; A. CZYRSKA- FILEMONOWICZ ; H. CIMENOGLU.** Fabrication of oxide layer on zirconium by micro-arc oxidation: Structural and antimicrobial characteristics. *Materials Science and Engineering,* 2017, vol. 71, 565 **[0003]**
- **F. MUHAFFEL ; G. CEMPURA ; M. MENEKSE ; A. CZYRSKA-FILEMONOWICZ ; N. KARAGULER ; H. CIMENOGLU.** Characteristics of multi-layer coatings synthesized on Ti6Al4V alloy by micro-arc oxidation in silver nitrate added electrolytes. *Surface and Coating Technology,* 2016, vol. 307, 308 **[0003]**
- **S. RYU ; SH HONG.** Corrosion Resistance and Antibacterial Properties of Ag-Containing MAO Coatings on AZ31 Magnesium Alloy Formed by Microarc Oxidation. *Journal of Electrochemical Society,* 2010, vol. 157, 131 **[0003]**
- **C. CHANG ; X. HUANG ; Y. LIU ; L. BAI ; X. YANG ; R. HANG ; B. TANG ; PK CHU.** High-current anodization: A novel strategy to functionalize titanium-based biomaterials. *Electrochimica Acta,* 2015, vol. 173, 345 **[0003]**
- **B.S. NECULA ; L.E. FRATILA-APACHITEI ; S.A. ZAAT ; I. APACHITEI ; J. DUSZCZYK.** In vitro antibacterial activity of porous TiO2-Ag composite layers against methicillin-resistant Staphylococcus ureus. *Acta Biomaterialia,* 2009, vol. 5, 3573 **[0003]**
- **D. TEKER ; F. MUHAFFEL ; M. MENEKSE ; NG KARAGULER ; M. BAYDOGAN ; H. CIMENOGLU.** Characteristics of multi-layer coating formed on commercially pure titanium for biomedical applications. *Materials Science and Engineering C,* 2015, vol. 48, 579 **[0003]**
- **X. ZHANG ; H. WANG ; J. LI ; X. HE ; R. HANG ; X. HUANG ; L. TIAN ; B. TANG.** Corrosion behavior of Zn-incorporated antibacterial TiO2 porous coating on titanium. *Ceramic International,* 2016, vol. 32, 919 **[0003]**
- **K. ROKOSZ ; T. HRYNIEWICZ ; L. DUDEK ; A. SCHUTZ ; J. HEEG ; M. WIENECKE.** Energy-Dispersive X-Ray Spectroscopy Mapping of Porous Coatings Obtained on Titanium by Plasma Electrolytic Oxidation in a Solution Containing Concentrated Phosphoric Acid with Copper Nitrate. *Advances in Materials Science,* 2016, vol. 16, 15 **[0003]**
- **I.V. LUKIYANCHUK ; I.V. CHERNYKH ; V.S. RUDNEV ; A. YU USTINOV ; L.M. TYRINA ; P.M. NEDOZOROV ; E.E. DMITRIEVA.** Catalytically active cobalt-copper-oxide layers on aluminium and titanium. *Protection of Metals and Physical Chemistry of Surfaces,* 2014, vol. 50, 209 **[0003]**
- **W. ZHU ; Z. ZHANG ; B. GU ; J. SUN ; L. ZHU.** Biological Activity and Antibacterial Property of Nano-structured TiO2 Coating Incorporated with Cu Prepared by Micro-arc Oxidation. *Journal of Materials Science & Technology,* 2013, vol. 29, 237 **[0003]**
- **K. ROKOSZ ; T. HRYNIEWICZ ; D. MATÝSEK ; S. RAAEN ; J. VALÍČEK ; L. DUDEK ; M. HARNIČÁROVÁ.** SEM, EDS and XPS Analysis of the Coatings Obtained on Titanium after Plasma Electrolytic Oxidation in Electrolytes Containing Copper Nitrate. *Materials,* 2016, vol. 9, 318 **[0003]**
- **X. YAO ; X. ZHANG ; H. WU ; L. TIAN ; Y. MA ; B. TANG.** Microstructure and antibacterial properties of Cu-doped TiO2 coating on titanium by micro-arc oxidation. *Applied Surface Science,* 2014, vol. 292, 944 **[0003]**
- **X. HUANG ; Y. LIU ; H. YU ; X. YANG ; Y. WANG ; R. HANG ; B. TANG.** One-step fabrication of cytocompatible micro/nano-textured surface with TiO2 mesoporous arrays on titanium by high current anodization. *Electrochimica Acta,* 2016, vol. 199, 116 **[0003]**

- **L. ZHANG ; J. GUO ; X. HUANG ; Y. ZHANG ; Y. HAN.** The dual function of Cu-doped TiO2 coatings on titanium for application in percutaneous implants. *Journal of Materials Chemistry,* 2016, vol. 4, 3788 **[0003]**