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

VERFAHREN ZUR HERSTELLUNG VON PORÖSEN ANTIBAKTERIELLEN BESCHICHTUNGEN AUF DER OBERFLÄCHE VON TITAN UND TITANLEGIERUNGEN

PROCÉDÉ DE FORMATION DE REVÊTEMENTS ANTIBACTÉRIENS POREUX SUR UNE SURFACE DE TITANE ET D'ALLIAGES DE TITANE

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- **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]**
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- **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**

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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, copper or zinc compounds, the obtained oxide layers are intended to be characterized 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 implantation processes. 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 the 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 0.00003-0.00400 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 the 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 behaviour 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.

[0004] 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

$Cu(NO_3)_2$. 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) describes the plasma electrochemical oxidation method using the bath containing 0.05 $mol \cdot dm^{-3}$ sodium β-glycerophosphate, 0.1 $mol \cdot dm^{-3}$ $Ca(CH_3COO)_2$ and 0.05 $mol \cdot dm^{-3}$ $(CH_3COO)_2Cu$. 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. Matysek, S. Raaen, J. Validek, L. Dudek, M. Harnicárová, Materials, 9 (2016) 318) there is known 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 $g \cdot dm^{-3}$ NaOH, 15 $g \cdot dm^{-3}$ NaH_2PO_4 and 3 $g \cdot dm^{-3}$ 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 $g \cdot dm^{-3}$ Na_3PO_4 and 1.0-8.0 $g \cdot dm^{-3}$ $Cu(NO_3)_2$. 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 $mol \cdot dm^{-3}$ sodium β-glycerophosphate, 0.02 $mol \cdot dm^{-3}$ $Ca(CH_3COO)_2$ and 0.00125-0.005 $mol \cdot dm^{-3}$ $Cu(CH_3COO)_2$.

[0005] The patent no. CN103911644 describes the plasma electrochemical oxidation of titanium alloys using baths containing phytic acid or phytate with the addition of electrolytes such as bioactive calcium, magnesium, zinc salts or with the addition of organic compounds such as tannic acid or hydroxides. Chromium(VI) compounds, fluorides and orthophosphates are not used during the process, therefore air polluting products have been limited. As a result of the process, microporous coating structures with good antibacterial properties, bioactivity, corrosion resistance and abrasion resistance are obtained. In the patent no. CN1035266261 there is presented the method of obtaining ceramic membranes containing zinc on the surface of titanium or magnesium modified by plasma electrochemical oxidation process using electrolytes containing soluble compounds of zinc and calcium, titanium or magnesium as anodes and stainless steel as cathode. The obtained ceramic membranes increase the bioactivity of the titanium or magnesium surface. Additionally, they degrade in the human body environment, causing the increase in immunity of human organism to bacterial infections and supporting the cell growth process in vitro. In the publication "Antibacterial activity and increased bone marrow stem cell functions of Zn-incorporated TiO2 coatings on titanium" (H. Hu, W. Zhang, Y. Qiao, X. Jiang, X. Liu, C. Ding, "Acta Biomaterialia" (8 (2012) 904) there is known the method of plasma electrochemical oxidation of titanium using the baths containing zinc. The bath containing 0.1 $mol \cdot dm^{-3}$ $C_4H_6O_4Ca \cdot H_2O$, 0.05 $mol \cdot dm^{-3}$ $C_3H_7Na_2O_6P \cdot 5H_2O$ and $Zn(CH_3COO)_2 \cdot 2H_2O$ in the concentration range 0.02-0.06 $mol \cdot dm^{-3}$ has been used. In the paper "SEM and EDS Characterization of Porous Coatings Obtained On Titanium by Plasma Electrolytic Oxidation in Electrolyte Containing Concentrated Phosphoric Acid with Zinc Nitrate" (K. Rokosz, T. Hryniewicz, K. Pietrzak, W. Malorny, "Advances in Materials Science" (17 (2017) 41), the titanium anodic oxidation method is described using the alkaline bath containing: 0.05 $mol \cdot dm^{-3}$ $C_3H_7Na_2O_6P \cdot 5H_2O$, 0.10 $mol \cdot dm^{-3}$ $Ca(CH_3COO)_2 \cdot H_2O$ and 0.04 $mol \cdot dm^{-3}$ $Zn(CH_3COO)_2 \cdot 2H_2O$, as well as the acid bath containing: 85% H_3PO_4 and 500 g of dissolved $Zn(NO_3)_2 \cdot 6H_2O$. The patent no. CN 107376897 describes the method of plasma oxidation of electrochemical titanium in the electrolyte containing zinc nanoparticles. In the manuscript "Preparation and photocatalytic performance of ZnO/WO3/TiO2 composite coatings formed by plasma electrolytic oxidation" (Q. Honglei, L. Chen, Y. Xiwen, W. Mingyue, Y. Zongcheng, "Journal of Materials Science: Materials in Electronics "(29 (2018) 2060) there is known the method of plasma oxidation of electrochemical titanium in the electrolyte containing zinc nanoparticles.

[0006] In the paper "Enhanced corrosion resistance and in-vitro biodegradation of plasma electrolytic oxidation coatings prepared on AZ91 Mg alloy using ZnO nanoparticlesincorporated electrolyte" (A. Bordbar-Khiabani, B. Yarmand, M. Mozafari, Surface and Coatings Technology (360 (2019) 153) there is described the method of plasma electrochemical oxidation in the bath containing 4.5 $g \cdot dm^{-3}$ of ZnO nanoparticles. In the manuscript "The effect of applied voltages on the structure, apatite-inducing ability and antibacterial ability of micro arc oxidation coating formed on titanium Surface" (Q. Du, D. Wei, Y. Wang, S. Cheng, S. Liu, Y. Zhou, D. Jia, Bioactive Materials (3 (2018) 426) there is presented the method

of plasma electrochemical oxidation using the bath consisting of 15 $g \cdot dm^{-3}$ EDTA, 8.8 $g \cdot dm^{-3}$ $Ca(CH_3COO)_2 \cdot H_2O$, 6.3 $g \cdot dm^3$ $Ca(H_2PO_4)_2 \cdot H_2O$, 7.1 $g \cdot dm^{-3}$ $Na_2SiO_3 \cdot 9H_2O$, 5 $g \cdot dm^{-3}$ NaOH, 6 $mL \cdot dm^{-3}$ H_2O_2 and 8.5 $g \cdot dm^{-3}$ $Zn(CH_3COO)_2$. The publication "Bactericidal activity and cytotoxicity of a zinc doped PEO titanium coating" (L. Sopchenski, K. Popat, P. Soares, "Thin Solid Films" (660 (2018) 477) presents the method of anodic electrochemical oxidation in the bath containing $Ca(CH_3COO)_2$, calcium glycerophosphate and $Zn(CH_3COO)_2$. The patent no. PL 225226 descibes the method of anodic electrochemical oxidation of tantalum, niobium and zirconium in the suspension of insoluble $CaSiO_3$ at a concentration of 1-300 $g \cdot dm^{-3}$ at the temperature of 15-50°C at the anodic current density of 5-200 $mA \cdot cm^{-2}$ and applied voltage of 100-650 V for 1-60 minutes. In the patent no. PL 225227 there is presented the method of electrochemical oxidation of plasma titanium and its alloys in a suspension of $CaSiO_3$ at a concentration of 1-300 $g \cdot dm^{-3}$ at the temperature of 15-50°C, at the anodic current density of 5-200 $mA \cdot cm^{-2}$ and applied voltage of 100-650 V in time 1-60 minutes. In the patent no. PL 396115 there is described the method of electrochemical oxidation of plasma titanium and its alloys in suspension containing $ZrSiO_4$ at the concentration of 1-100 $g \cdot dm^{-3}$ with the addition of the alkali metal hydroxide at the concentration of 5-100 $g \cdot dm^{-3}$ at the temperature of 15-50°C, at the anodic current density 5-500 $mA \cdot cm^{-2}$ and 1-600 V for 1-30 minutes. The patent no. PL 214630 describes the method of electrochemical plasma oxidation of Ti-xNb-yZr alloys in the $Ca(H_2PO_2)_2$ solution at the concentration of 1-150 $g \cdot dm^{-3}$ or in a NaH_2PO_2 solution at a concentration of 1-250 $g \cdot dm^{-3}$ at the temperature of 15-50°C, at the anodic current density of 5-5000 $mA \cdot cm^{-2}$ and applied voltage of 100-650 V for 1-60 minutes. The paper "Surface characterisation of Ti-15Mo alloy modified by a PEO process in various suspensions" (A.Kazek-Kesik, G. Dercz, I. Kalemba, K.Suchanek, A. Kukharenko, D. Korotin, J. Michalska, A. Krzqkala, J.Piotrowski, E. Kurmaev, S. Cholakh, W. Simka, Materials science and engineering, vol.39 (2014)) reports on the surface modification of a Ti-15Mo alloy by plasma electrolyticoxidation (PEO). This process was carried out in solutions of 0.1 M $Ca(H_2PO_2)_2$ with various concentrations of tricalcium phosphate ($Ca_3(PO_4)_2$), wollastonite ($CaSiO_3$), or silica (SiO_2) using voltages of up to 350V. The surface microstructure (SEM, cross-section of coating), roughness and chemical composition (energy dispersive X-ray spectroscopy, thin layer X-ray diffraction, X-ray photo electron spectroscopy and Raman spectroscopy) of the porous oxide layers were investigated. The concentration of powder added to the solution changed the chemical composition and morphology of PEO coatings on the Ti-15Mo alloy surface. Calcium and phosphorous compounds were detected in the coatings formed on the substrate by the PEO process at 300V.

[0007] The aim of the invention is to develop a method allowing to obtain the porous oxide layers with incorporated compounds with antibacterial properties.

[0008] The essence of the invention is a method of titanium surface modification by plasma electrochemical oxidation in aqueous $Ca(H_2PO_2)_2$ baths at a concentration from 0.01 $mol \cdot dm^{-3}$ to 5 $mol \cdot dm^{-3}$ with an anodic current density from 1 $mA \cdot cm^{-2}$ to 250 $mA \cdot cm^{-2}$ and applied voltage from 50 V to 600 V, by immersing the element which surface is to be modified in the aqueous $Ca(H_2PO_2)_2$ solution, characterized in that the bath comprises insoluble particles of metal phosphate at a concentration from 1 $g \cdot dm^{-3}$ to 400 $g \cdot dm^{-3}$, and the aqueous salt solution contains copper(II) phosphate $Cu_3(PO_4)_2$ at a concentration from 1 $g \cdot dm^{-3}$ to 400 $g \cdot dm^{-3}$ or the aqueous salt solution contains silver(I) phosphate Ag_3PO_4 at a concentration from 1 $g \cdot dm^{-3}$ to 400 $g \cdot dm^{-3}$ or the aqueous salt solution contains zinc phosphate $Zn_3(PO_4)_2$ at a concentration from 1 $g \cdot dm^{-3}$ to 400 $g \cdot dm^{-3}$.

[0009] 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. An 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.

[0010] Example I: The titanium implant, pre-treated by polishing, degreasing, etching and rinsing in demineralised water is placed in the solution containing 0.1 $mol \cdot dm^{-3}$ $Ca(H_2PO_2)_2$ and the suspension of 10 $g \cdot dm^{-3}$ Ag_3PO_4. 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 $mA \cdot cm^{-2}$. 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.

[0011] 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 $mol \cdot dm^{-3}$ $Ca(H_2PO_2)_2$ and the suspension of 100 $g \cdot dm^{-3}$ $Cu_3(PO_4)_2$. 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 $mA \cdot cm^{-2}$. 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.

[0012] 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} $Zn_3(PO_4)_2$. 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 aqueous $Ca(H_2PO_2)_2$ 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 by immersing the element which surface is to be modified in the aqueous $Ca(H_2PO_2)_2$ solution **characterized in that** the bath comprises insoluble particles of metal phosphate at a concentration from 1 g·dm^{-3} to 400 g·dm^{-3}, and the aqueous salt solution contains copper(II) phosphate $Cu_3(PO_4)_2$ at a concentration from 1 g·dm^{-3} to 400 g·dm^{-3} or the aqueous salt solution contains silver(I) phosphate Ag_3PO_4 at a concentration from 1 g·dm^{-3} to 400 g·dm^{-3} or the aqueous salt solution contains zinc phosphate $Zn_3(PO_4)_2$ at a concentration from 1 g·dm^{-3} to 400 g·dm^{-3}.

Patentansprüche

1. Verfahren zur Oberflächenmodifizierung von Titan durch plasmaelektrochemische Oxidation in wässrigen $Ca(H_2PO_2)_2$-Bädern mit einer Konzentration von 0,01 mol/dm^{-3} bis 5 mol/dm^{-3} mit einer anodischen Stromdichte von 1 mA/cm^{-2} bis 250 mA/cm^{-2} und einer angelegten Spannung von 50 V bis 600 V durch Eintauchen des Elements, dessen Oberfläche modifiziert werden soll, in die wässrige $Ca(H_2PO_2)_2$-Lösung, **dadurch gekennzeichnet, dass** das Bad unlösliche Metallphosphatteilchen in einer Konzentration von 1 g/dm^{-3} bis 400 g/dm^{-3} enthält, und die wässrige Salzlösung Kupfer(II)-phosphat $Cu_3(PO_4)_2$ in einer Konzentration von 1 g/dm^{-2} bis 400 g/dm^{-3} oder die wässrige Salzlösung Silber(I)-phosphat Ag_3PO_4 in einer Konzentration von 1 g-dm" bis 400 g-dm" oder die wäßrige Salzlösung Zinkphosphat $Zn_3(PO_4)_2$ in einer Konzentration von 1 g/dm^{-3} bis 400 g/dm^{-3}.

Revendications

1. Méthode de modification de la surface du titane par électrochimie au plasma dans des bains aqueux de $Ca(H_2PO_2)_2$ à une concentration de 0.01 mol dm^{-3} à 5 mol dm^{-3} avec une densité de courant anodique de 1 mA cm^{-2} à 250 mA cm^{-2} et une tension appliquée de 50 V à 600 V en immergeant l'élément dont la surface doit être modifiée dans la solution aqueuse de $Ca(H_2PO_2)_2$ **caractérisée par le fait que** le bain comprend des particules insolubles de phosphate métallique à une concentration de 1 g dm^{-3} à 400 contenant du zinc phosphate $Zn_3(PO_4)_2$ à une concentration de 1 g dm^{-3} à 400 g dm^{-3}, et la solution saline aqueuse contient du phosphate de cuivre (II) $Cu_3(PO_4)_2$ à une concentration de 1 g dm^{-3} à 400 g dm^{-3} ou la solution saline aqueuse contient du phosphate d'argent (I) Ag_3PO_4 à une concentration de 1 g dm^{-3} à 400 g dm^{-3} ou la solution saline aqueuse contient du phosphate de zinc $Zn_3(PO_4)_2$ à une concentration de 3 g dm^{-3} à 400 g dm^{-3}.

REFERENCES CITED IN THE DESCRIPTION

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- CN 108543109 **[0003]**
- CN 103911644 **[0005]**
- CN 1035266261 **[0005]**
- CN 107376897 **[0005]**
- PL 225226 **[0006]**
- PL 225227 **[0006]**
- PL 396115 **[0006]**
- PL 214630 **[0006]**

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