CALCIUM PHOSPHATE FILM ON NIOBIUM SUBSTRATE OBTAINED BY TWO-STEP OXIDATION

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Introduction: The niobium (Nb) is a non-toxic element[1] and can be used in the implant since they have excellent corrosion resistance[2] and good biological compatibility in soft and hard tissues [3][4]. To achieve osteointegration, niobium requires a suitable surface like anodization and plasma electrolytic oxidation (PEO)[4]. In the present work, niobium substrates were electrochemically treated in two steps and the morphology, chemical composition, crystal systems, wettabilty and film adhesion were analyzed. Materials and Methods: Nb samples of 20 x 15 x 1 mm3 were obtained from 98.8% niobium sheet. All oxidations were carried out with a Nb counter-electrode bar under potentiostatic mode and electrolyte agitation at room temperature. The following electrolytes were prepared to oxidize the Nb surfaces: 1. P electrolyte = phosphoric acid 0.8 mol.L-1 + H2O2 3 mol.L-1; 2. Ca electrolyte = 0.5 mol.L-1 Ca (CH3CO2)2.H2O; Mixture of P and Ca electrolytes with the proportions, both in volume: • P electrolyte 50 % + Ca electrolyte 50 %; • P electrolyte 25 % + Ca 75 % electrolyte. The procedure of the oxidation treatment in two-step involves two separate successive processes. The first step consisted in to create a pre-layer oxidizing all Nb samples in P electrolyte under 200 V for 60 s, then, they were washed in distilled water; secondly, the pre-layers were re-oxidized for 60 s under following parameters: 1. 270 V using Ca electrolyte (270V/Ca sample); 2. 350 V using P + Ca mixture electrolyte (350V/P+Ca sample); 3. 350 V using P 25 % + Ca 75 % mixture electrolyte (350V/P25%+Ca75% sample). The film adhesion on the substrate was evaluated by nanoscratch test. Oxidized surface and nanoscratch morphologies were analyzed by Scanning electron microscopy. The crystalline phases were identified by X-ray diffraction (XRD). The chemical compositions were obtained by EDS-energy dispersive spectroscopy. Average surface roughness (Ra) was measured by a profilometer. The contact angle measurement was performed with a goniometer by sessile drop technique, using 1 µL of distilled water. Results: All films showed porous surfaces containing calcium, phosphorus, and higher hydrophilicity than the niobium polished. Roughness average measured, remained in the sub-micrometric range. The XRD patterns identified peaks assigned to orthorhombic Nb2O5 and identified apatite presence in oxidations that containing higher proportions of Ca electrolyte. Nanoscratch tests display that samples with apatite on the surface presented wide and deep trails. However, also the better results as exposure of substrate (they had rare or no exposure the metallic substrate). Discussion: All two-step oxidized niobium surface demonstrated great features for applications in the osteointegration processes: the favorable chemical composition that increases the biocompatibility[5]; hydrophilicity[6]; crystalline niobium pentoxide (orthorhombic)[7] and crystalline calcium phosphate (apatite)[7]. The poor mechanical properties of apatite limit its application. A good way to fix this is to cover metallic implants with hydroxyapatite [8], like the surfaces produced on niobium by two-step oxidation process. Conclusion: Two-step oxidation is a simple, inexpensive and fast technique and analyzing the set of surface features obtained, we can to allege that these surfaces have potentially a promising use in osteointegrable implants. Acknowledgements: 1. Centro de Microscopia Eletrônica (CME) 2. Laboratório de ótica de raios X e instrumentação (LORXI) References: 1. Dsouki, N. A. et al. Cytotoxic, hematoletic and histologic effects of niobium pentoxide in Swiss mice. J. Mater. Sci. Mater. Med. 25, 1301–5 (2014) 2. Matsuno, H., Yokoyama, A., Watari, F., Uo, M. & Kawasaki, T. Biocompatibility and osteogenesis of refractory metal implants, titanium, hafnium, niobium, tantalum and rhenium. Biomaterials 22, 1253–1262 (2001). 3. Eisenbarth, E., Velten, D., Müller, M., Thull, R. & Breme, J. Nanostructured niobium oxide coatings influence osteoblast adhesion. J. Biomed. Mater. Res. A 79, 166–75 (2006). 4. Neupane, M. P., Park, I. S. & Lee, M. H. Surface characterization and corrosion behavior of micro-arc oxidized Ti surface modified with hydrothermal treatment and chitosan coating. Thin Solid Films 550, 268–271 (2014) 5. Lugovskoy, A. & Lugovskoy, S. Production of hydroxyapatite layers on the plasma electrolytically oxidized surface of titanium alloys. Mater. Sci. Eng. C. Mater. Biol. Appl. 43, 527–32 (2014) 6. Bhat, V. & Balaji, S. S. Surface topography of dental implants. Nitte Univ. J. Heal. Sci. 4, (2014). 7. Miyazaki, T., Kim, H., Kokubo, T., Ohtsuki, C. & Nakamura, T. Apatite-Forming Ability of Niobium Oxide Gels in a Simulated Body Fluid. J. Ceram. Soc. Japan 109, 929–933 (2001) 8. Choudhury, P. & Agrawal, D. C. Nanomedicine. (Elsevier, 2012). doi:10.1533/9780857096449.1.84