Fabrication and characterization of porous coatings containing copper on a titanium substrate, using plasma electrolytic oxidation

ABSTRACT

In the frame of doctoral thesis, the fabrication and characterization of porous coatings enriched in copper, obtained by plasma electrolytic oxidation (PEO) in new electrolytes based on concentrated orthophosphoric acid and copper(II) nitrate(V) trihydrate, were presented. For characterization and description of the obtained coatings the following techniques were used: scanning electron microscopy (SEM), confocal laser scanning microscopy (CLSM), energy-dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), X-ray diffractometry (XRD), glow discharge optical emission spectroscopy (GDOES) and potentiodynamic polarization (PDP). The obtained results allowed to propose mathematical models taking into account the influence of PEO process conditions, such as chemical composition of electrolytes and interelectrode voltage, on selected 3D parameters used for description of surface roughness (Sp, Sv, Sz, Sa) and chemical composition of obtained coatings (in the nano scale - based on the conducted XPS, and micro scale - based on EDS, XRD). The XRD research allowed to propose models explaining the method of coatings formation in the PEO process, demonstrating the possibility of introducing copper ions into the PEO coatings in the form of crystalline and nanocrystalline or amorphous compounds. On the basis of XPS results, on may state that the composition of the top 10 nm nanolayer includes, inter alia, Ti^{4+}, Cu^{+}, Cu^{2+} and most likely the following phosphate groups: PO_4^{3-}, and/or $P_2O_7^{4-}$, and/or PO_3^{-}, and/or $H_2PO_4^{-}$, and/or HPO_4^{2-}, and/or $HP_2O_7^{3-}$, and/or $H_2P_2O_7^{2-}$, and/or $H_3P_2O_7^{-}$. The description of the surface stereometry of the obtained coatings allows to indicate two processes of PEO coating formation related to the creation of the coating with a primary structure and secondary structure. These findings were supported by the presented in PhD thesis mathematical models. Elemental depth profiles obtained by means of GDOES method allowed to determine average thicknesses of porous coatings, and they were in the range from 7.0 μm to 27.8 μm. Layer models of the PEO coatings, obtained in electrolytes based on concentrated orthophosphoric acid and copper(II) nitrate trihydrate, have been proposed. The conducted research allows to prove that the PEO coatings, obtained at voltages in the range from 450 to 650 V in electrolytes based on concentrated orthophosphoric acid with the addition of copper(II) nitrate trihydrate, can be described by a three-layer model that includes porous layer, semi-porous layer and transition layer. It was also shown that there are positive correlations both between the PEO voltage and content of copper(II) nitrate(V) trihydrate and the chemical composition expressed by the Cu/P atomic ratio. It was assumed that the highest recorded average value of Cu/P for entire thickness of PEO coating was 0.24 ± 0.04 and for surface nanolayer was ranging from 0.008 to 0.098. Based on the PDP results, regarding the obtained PEO coatings, it has been shown that using the interelectrode voltage of 450 V provides a better electrochemical repeatability of obtained coatings than for those ones obtained at higher voltages.

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