

Fabrication and studies of porous coatings containing calcium, magnesium and zinc on a titanium substrate for mechanical engineering applications

ABSTRACT

In the doctoral dissertation, the porous coatings enriched with calcium, magnesium and zinc, fabricated on titanium substrate by plasma electrolytic oxidation processes under the DC and AC conditions with voltage control, in electrolytes based on concentrated phosphoric acid with selected nitrates, are presented. It has been noticed that the change of the DC-PEO or AC-PEO processes voltages, treatment times, as well as the electrolytes' compositions allows to fabricate coatings with the desired stereometric, as well as chemical and electrochemical properties. Based on the CLSM (confocal laser scanning microscopy) studies, it was found that the surface development described by the developed interfacial area ratios (Sdr parameter) of porous coatings obtained by the DC-PEO process were in the range from 277% up to 2357%, while the application of the AC voltage resulted in formation of porous coatings with a much lower surface development within the range from 44% up to 166%.

The XPS (X-ray photoelectron spectroscopy) tests of top nano-layers of coatings produced on the titanium substrate using the DC-PEO or AC-PEO methods indicated that, dependent on the electrolyte used, containing one, two or three nitrates(V), the following contents of calcium (1.9 - 4.7 at.%), magnesium (2.3 - 10.9 at.%), zinc (0.2 - 1.3 at.%), titanium (2.1 - 6.3 at.%) and phosphorus (22.5 - 31.9 at.%), as well as oxygen (57.4 - 68.6 at.%), were detected. Based on the available XPS standards, it can be concluded that the nanolayers are composed mainly of phosphates of selected metals from the electrolyte (Ca^{2+} , Mg^{2+} , Zn^{2+}) as well as from the substrate (Ti^{4+}).

The XRD (x-ray diffraction) measurements performed on the coatings obtained by DC-PEO processes, have shown that an increase of crystalline-to-amorphous phase ratio can be obtained by rising the PEO voltage or shortening the processing time. In the AC-PEO process with the use of two cathodic voltages, i.e. -35 V and -85 V, there were no crystalline phases recorded in the fabricated coatings, while for -135 V the titanium oxides (TiO and Ti_3O) were found.

The depth profiles obtained by the GDEOS (glow-discharge optical emission spectroscopy) method show that the increase of DC voltage from 500 V up to 650 V results in doubling thickness

of the coatings, while the treatment time increasing effects in the halving of their thickness. On the other hand, the use of the AC-PEO process leads to the production of coatings with much smaller thicknesses, not exceeding 4 μm . The application of the -35 V cathode voltage resulted in obtaining coatings with thicknesses in the range of 1-3 μm , and the change in the cathode voltage to -135 V effected in the coatings with many times smaller thicknesses.

Corrosion tests indicate no significant differences in the values of the passivation current density of DC-PEO coatings obtained under the process times of 1, 3 and 5 min, what was also observed regarding the used voltages of 500 V and 575 V. However, the usage of the DC voltage of 650 V results in obtaining coatings characterized by passivation currents densities higher than those ones obtained at lower voltages. The use of voltage (+400, -35) V in the AC-PEO process results in getting coatings characteristic by significantly lower passivation current density than for coatings obtained at the voltage of (+400, -135) V.