

Anodic Titanium Oxides Grown in Sulphuric and Phosphoric Acid Electrolytes

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INTRODUCTION: Depending on the electrolyte, its concentration and the applied potential, anodic oxide films on Ti can grow mostly dense or porous, amorphous or crystalline [1, 2]. Such films are frequently used for biomedical surface preparation. They are thought to protect the un-noble substrate from corrosion and enhance its biocompatibility, while the thickness dependent interference colors allow for color-coding of implantable devices. In the present study, growth mechanism and oxide morphology upon anodization of Ti in sulfuric and phosphoric acid electrolytes is investigated with non-destructive ac impedance spectroscopy (EIS), transmission electron microscopy (TEM) and Raman analysis. Chemical depth profiling is performed by glow-discharge optical emission spectroscopy (GD-OES), X-ray photoelectron spectroscopy (XPS), and Rutherford backscattering (RBS) combined with elastic recoil detection analysis (ERDA).

METHODS: C.p. Ti discs (grade 2) were used. Anodic oxidation (5 V/s) was performed up to different end potentials in 1 M H₂SO₄ or 1 M H₃PO₄ at 25°C. EIS was done using an Autolab PGSTAT30 with FRA module. Raman spectra were measured in backscattering geometry on a Renishaw Ramascope 2000 using a HeNe-laser. Ellipsometry was performed on a spectroscopic ellipsometer (MOSS model ES 4G). TEM was performed on Philips CM-300 and EM-430 microscopes at 300 keV. GD-OES (Jobin-Yvon 5000 RF) was used for estimation of film thickness and chemical depth profiling. RBS and ERDA spectra were obtained by irradiation with a 2 MeV He-ion beam on a Van de Graaff accelerator.

RESULTS: For a given potential, oxides grown in H₃PO₄ are slightly thinner than in H₂SO₄. Already at 10 V, a small amount of anatase is observed in the Raman signal of both oxide types. For a given potential the crystallization is found more progressed in H₂SO₄ than in H₃PO₄. TEM observations reveal a multilayer structure consisting of a porous central part and a dense part, already observed at 20 V (Fig. 1). Besides the higher amount of crystalline phase in H₂SO₄, a significant difference in the location of first nanocrystallites is observed in both oxide types. While crystallites are present around the central porous part and in the outermost dense part in H₂SO₄ oxides, nanocrystals are exclusively found

at the interface metal/oxide in H₃PO₄. The film porosity is confirmed by the appearance of a 2nd capacitance in impedance spectra above 20 V. Based on TEM, a 2-layer model is chosen for data fitting. The ongoing crystallization with increasing potential can be correlated to systematic changes in resistances and capacitances. Impedance data confirm the slower crystallization in H₃PO₄.

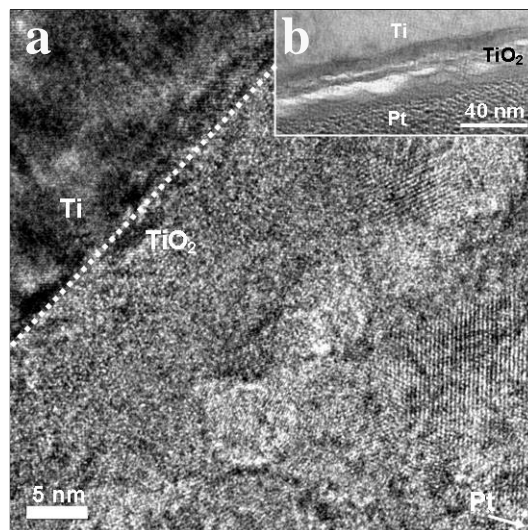


Fig.1 (a) TEM bright field image of a 20 V sulfuric acid oxide. (b) Overview of its layered structure.

XPS on 80 V oxides reveal stoichiometric TiO₂. A S contamination located at the metal/oxide interface (max. 2.5 at-%) and a P peak at the surface, rapidly decreasing to around 5 at-% inside the oxides, are found. An accumulation of H around the interface metal/oxide is seen by GD-OES, the maximum concentration being quantified to 20-30 at-% by RBS/ERDA. Ion beam analysis allows to estimate the film porosity to 34-38%.

DISCUSSION & CONCLUSIONS: Crystallization of anodic oxides on Ti is found to start at potentials as low as 10 V, strongly influencing the fitted capacitance and resistance values obtained from ac impedance data. The presence of a porous layer is observed at potentials as low as 20 V by TEM and EIS. Further crystallization is found to progress slower in H₃PO₄ than in H₂SO₄.

REFERENCES: ¹ Y.-T. Sul et al., Med. Eng. Phys., 23 (2001) 329. ² J. Marsh, D. Gorse, Electrochim. Acta, 43 (7) (1998) 659.

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