

## Electrolytic Deposition of Valve Metal Oxide Thin Films as Interference Coatings on Biomedical Implants

P. Kern, P. Schwaller, J. Michler

EMPA, Materials Technology Section, Thun, Switzerland

**INTRODUCTION:** Electrolytic deposition is an important, cost-effective tool in the formation of metallic, ceramic or organic films, including nanostructured materials and monolayers. Recently, great interest has emerged in electrolytic deposition of oxide films such as  $\text{TiO}_2$ ,  $\text{Nb}_2\text{O}_5$  and  $\text{ZrO}_2$  [1,2]. Such films are highly attractive for photovoltaic, electronic, electrochemical and sensor (e.g. oxygen sensor) applications. Furthermore, the excellent biocompatibility and the thickness dependent interference color predefine these oxide films for biomedical applications, e.g. for color-coded biocompatible layers on non-anodizable biomedical alloys.

**METHODS:** Thin  $\text{TiO}_2$ ,  $\text{Nb}_2\text{O}_5$  and  $\text{ZrO}_2$  films were electrolytically deposited on AISI 316L, Ti6Al4V and CoCrMo substrates via hydrolysis of peroxocomplexes by electrogenerated base using  $\text{TiCl}_4$ ,  $\text{NbCl}_5$  and  $\text{ZrOCl}_2$  salts in methanol/water mixtures. Deposition occurred statically at  $0^\circ\text{C}$  using a simple 2-electrode setup and a computer-controlled power source. Post-heat treatment of the as-deposited metal-peroxide films lead to densification and crystallization. Film morphology and structure were analyzed by SEM, TEM and Raman. The chemical composition was assessed by quantitative depth profiling with glow discharge optical emission spectrometry (GD-OES). Nanoindentation and nanoscratch tests were performed using a MTS Nanoindenter XP with a Berkovich diamond tip.

**RESULTS:** Optimization of electrolyte formulation and deposition parameters lead to stoichiometric titania films with almost uniform thickness and hence, thickness-dependent interference colors, similar as known from the color-anodization process of Ti-alloys. Crack-free films were found up to 140 nm on AISI 316L and up to 190 nm on Ti6Al4V substrates. After thermal annealing at  $450^\circ\text{C}$  of as-deposited amorphous peroxotitanium hydrate films, Raman and TEM showed highly stoichiometric, nano-crystalline anatase films. GD-OES showed dehydration and densification during heat treatment and revealed stoichiometric  $\text{TiO}_2$  films on AISI 316 L with small Fe (3-4 at-%) and Cr (1 at-%) contamination due to thermal diffusion from the substrate. On the Ti6Al4V substrates, the comparison between

electrolytic  $\text{TiO}_2$  films and color-anodization in sulfuric and phosphoric acid containing electrolytes showed significant higher purity of electrolytic films, absent of V, Al, S, P contaminations as found in anodic oxides (4-6 at-% Al, 1-2 at-% V). Annealing greatly increased the mechanical properties of the green films. A hardness of 5.5 - 6.6 GPa ( $\text{TiO}_2$ ), excellent adhesion and very ductile behavior during scratch tests were found from nanoindentation and scratch tests.  $\text{Nb}_2\text{O}_5$  and  $\text{ZrO}_2$  thin films were crystalline and stoichiometric, but the higher annealing temperature ( $600^\circ\text{C}$ ), chosen based on DTA/TG measurements, lead to grain growth and deteriorated performance in scratch tests, requiring further optimization.

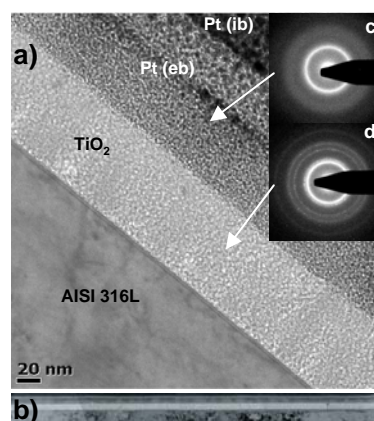


Fig. 1(a) TEM micrograph of annealed electrolytic  $\text{TiO}_2$  film on AISI 316L. (b) Overview of thickness uniformity.

**DISCUSSION & CONCLUSIONS:** Based on thickness uniformity, high purity and good mechanical properties, electrolytic  $\text{TiO}_2$  films are not only attractive as biocompatible colored coatings on non-anodizable biomedical alloys such as AISI 316 and CoCrMo, but also for Ti-alloys that are often anodized for protective as well as coding reasons prior to implantation.

**REFERENCES:** <sup>1</sup> I. Zhitomirsky, *J. Europ. Ceram. Soc.*, 19, (1999) 2581. <sup>2</sup> P. Kern et. al, submitted to *Thin Solid Films*, (2005).

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