

Electrolytic deposition of titania films as interference coatings on biomedical implants: Microstructure, chemistry and nano-mechanical properties

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Abstract

TiO₂ films with uniform thickness were electrolytically deposited on AISI 316L stainless steel and Ti6Al4V substrates for potential use as color coded biocompatible coatings on biomedical implants. Deposition occurred via a peroxoprecursor method from solutions containing TiCl₄ and H₂O₂. By optimizing electrolyte formulation and deposition parameters, thin stoichiometric titania films with almost uniform thickness-dependent interference colors, similar as known from the color anodization processes of Ti-alloys, were obtained. 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 °C of as-deposited amorphous peroxotitanium hydrate films, Raman and transmission electron microscopy showed highly stoichiometric, nanocrystalline anatase films. Chemical depth profiling was performed by glow-discharge optical emission spectrometry (GD-OES), showing clearly a densification and loss of water during annealing. On AISI 316L, GD-OES revealed stoichiometric TiO₂ films containing a small Fe (3–4 at.%) and Cr (1 at.%) contamination due to thermal diffusion from the substrate. On Ti6Al4V, the comparison between electrolytic TiO₂ films and color-anodization in different sulfuric and phosphoric acid containing electrolytes showed significant higher purity of electrolytic films, absent of V, Al, S, P contaminations as they were found in anodic oxides (4–6 at.% Al, 1–2 at.% V), especially V and S being problematic in biomedical applications. Annealing greatly increased the mechanical properties of the green films. A nano-hardness of 5.5–6.6 GPa, elastic modules close to substrate modules, excellent adhesion and very ductile behavior were found from nanoindentation and scratch tests. Based on thickness uniformity, high purity and good mechanical properties, electrolytic TiO₂ films are not only attractive as biocompatible colored coatings on non-anodizable biomedical alloys such as AISI 316L and CoCrMo, but also for Ti-alloys that are anodized for protective as well as coding reasons prior to implantation.

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1. Introduction

The manifold properties of thin titania films are of considerable interest for photovoltaic, electronic, catalytic, electrochemical and sensor (e.g. oxygen sensor) applications. Furthermore, its self-cleaning and disinfecting properties under UV exposure, its excellent biocompatibility and its thickness-dependent interference color predefine TiO₂ films for biomedical applications.

Among various conventional methods such as physical and chemical vapor deposition, as well as sol–gel processes, electrodeposition offers a number of combined advantages for deposition of thin ceramic films, owing to simple and low cost equipment, rigid control of film thickness, composition and

deposition rate, low temperature process nature and the possibility of film formation on substrates of complicated shape.

The use of inorganic salts of Ti in aqueous electrolytic solutions is a problem, since it is accompanied by hydrolyzation to form Ti hydroxide precipitates, requiring for deposition in very acidic and sometimes even oxygen-free environment, e.g. when working with TiCl₃ [1,2]. The problem of solution precipitation may be avoided when depositing using a sacrificial Ti anode in acetone [3,4], but the volatility of the electrolyte, the incorporation of iodine in the deposit as well as the limitations in deposition of oxides with complex stoichiometry form disadvantages. Using (NH₄)₂[TiO(C₂O₄)₂] as a complex organic Ti-precursor [5,6], deposition can be achieved at pH 4 in aqueous environment. However, no information on deposit morphology and purity is provided by the authors. A very promising route for deposition of thin oxide films in aqueous environment is the peroxoprecursor method using

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TiCl₄ [7–12] or TiOSO₄ [13] as starting material in presence of hydrogen peroxide. Zhitomirsky and co-workers have demonstrated the successful deposition of thin TiO₂ [7–12], Nb₂O₅ [10,14], ZrO₂ [7,8], Y₂O₃ [15], ZrTiO₄ [8] and PbZrO₃ [7] films without degassing the electrolyte. These authors deposited TiO₂ on platinum, silicon, platinized silicon and graphite substrates. Unfortunately, no information on deposit thickness uniformity, interference color, mechanical properties and very little information on purity of obtained films is available.

Exactly these issues are critical when considering electrolytic TiO₂ thin films for color coding and enhancement of biocompatibility of biomedical implants made of stainless steel, CoCrMo or Ti-alloys. In the present paper, using the Tiperoprecursor method, we investigated the possibility of depositing TiO₂ thin films, having macroscopically uniform thickness and stoichiometry and hence, uniform interference color, on biomedically relevant AISI 316L and Ti6Al4V substrates. We optimized electrolyte and deposition conditions and investigated structure, morphology, chemistry and nano-mechanical properties of obtained titania films.

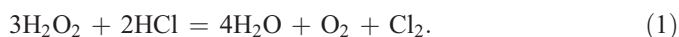
2. Experimental details

2.1. Substrate preparation

Metal discs (15 mm diameter, 1 mm thickness) of AISI 316L stainless steel and Ti6Al4V (grade 5) were mechanically polished to a mirror finish to facilitate later quantitative depth profilometric and nanomechanical analysis of electrolytic deposits. Before deposition, all substrates were ultrasonically cleaned and activated in acetone, ethanol and piranha solution (H₂SO₄/H₂O₂=3/1 vol.%) followed by copious rinsing with ultrahigh-purity water (18 MΩ cm).

2.2. Electrolytes and deposition

Various solutions containing TiCl₄ and H₂O₂ in mixed solvents of methanol, ethanol and water were tested. The influence of salt and peroxide concentration, solvent chemistry, pH, temperature and deposition current density was studied. Best film uniformity was obtained in 0.05 M TiCl₄ (Fluka), 0.5 M H₂O₂ in a mixed methanol/water (3:1 vol.%) solvent (pH=0.97). All chemicals were ACS grade. The procedure for electrolyte preparation consisted of slow addition of the metal salt to half of the final solvent volume, slow addition of hydrogen peroxide and subsequent adjustment to the final volume. Electrolytes were stored in the fridge at 4 °C right after preparation and pH measurement. During addition of H₂O₂ an immediate color change from transparent to dark orange was observed, indicating formation of a peroxo-complex [7,13]. The color change was followed by slight gas evolution, probably due to an oxireduction process [10,16]



The working electrode was fixed to a Teflon holder, facing up and leaving a small recess ($d=1$ mm) on the exposed surface ($A=1.33$ cm²). In order to avoid bubble problems, the

Teflon holder vibrated during deposition. Electrodeposition was performed galvanostatically up to the desired charge, working at 0 °C. Due to the high resistivity of the deposited thin films leading to deposition potentials up to 30 V, a Labview controlled high power source (Xantrex XDC 300-20) was used for deposition rather than an analytical potentiostat, working in a 2-electrode setup containing a large hemicylindrical Pt mesh as counter electrode. The applied current was precisely read back over selectable shunt resistors. Typical deposition currents were in the order of 20–110 mA cm⁻².

2.3. Heat treatment

After evacuating the oven (Gero GLO 120/11-1G) and flooding with high purity argon, thermal annealing was performed starting from room temperature with a heating rate of approximately 200 °C/h and a hold time of 1 h at 450 °C, followed by fan assisted cooling at approximately 400 °C/h.

2.4. Raman

Laser Raman spectra were obtained in backscattering geometry with a Renishaw Ramascope 2000 using a 633 nm HeNe laser and a spot size of approximately 5 μm.

2.5. Focussed ion beam lamella preparation and electron microscopy

A transmission electron microscope (TEM) lamella was prepared by focused ion beam (FIB) milling. The final lamella was approximately 150 nm thick. Thin film structure and morphology was studied with TEM at 300 kV (Philips CM30). Surface morphology and mechanical behavior during scratch tests were studied by scanning electron microscopy (SEM, Hitachi HF-4800). Energy dispersive X-ray (EDX) analysis was performed on the TEM lamella using the HF-4800 working at 30 kV.

2.6. Glow-discharge optical emission spectrometry (GD-OES)

The Yobin–Yvon 5000 RF was equipped with a 4 mm r.f.-glow discharge source, a polychromator and a monochromator optical spectrometer. The calibration file was based on various reference materials for all detected elements, including titanium alloys, and several anodized Ti, TiAlV and TiAlNb substrates with known oxide composition from X-ray photoelectron spectroscopy (XPS) data (Ti/O ratio, Al, V, Nb) and known thickness from TEM observation. Before each set of GD-OES experiments, an anodized Ti-alloy reference sample with known thickness and composition was re-measured for compensation of daily variations of the sputter rate. Best crater shape and plasma starting conditions were found at 700 Pa, 25 W (modulus=680, phase=440). Prior to GD-OES experiments, all samples were cleaned in acetone, ethanol and ultrapure water, dried and immediately covered with a thin evaporated gold layer to get sharp information from the surface of the oxide.

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