

Transmission electron microscopy of coatings formed by plasma electrolytic oxidation of titanium

E. Matykina, R. Arrabal, P. Skeldon*, G.E. Thompson

Corrosion and Protection Centre, School of Materials, The University of Manchester, Sackville Street, P.O. Box 88, Manchester M60 1QD, UK

Received 18 July 2008; received in revised form 3 October 2008; accepted 8 October 2008

Available online 25 October 2008

Abstract

Transmission electron microscopy and supporting film analyses are used to investigate the changes in composition, morphology and structure of coatings formed on titanium during DC plasma electrolytic oxidation in a calcium- and phosphorus-containing electrolyte. The coatings are of potential interest as bioactive surfaces. The initial barrier film, of mixed amorphous and nanocrystalline structure, formed below the sparking voltage of 180 V, incorporates small amounts of phosphorus and calcium species, with phosphorus confined to the outer ~63% of the coating thickness. On commencement of sparking, calcium- and phosphorus-rich amorphous material forms at the coating surface, with local heating promoting crystallization in underlying and adjacent anodic titania. The amorphous material thickens with increased treatment time, comprising almost the whole of the ~5.7- μm -thick coating formed at 340 V. At this stage, the coating is ~4.4 times thicker than the oxidized titanium, with a near-surface composition of about 12 at.% Ti, 58 at.% O, 19 at.% P and 11 at.% Ca. Further, the amount of titanium consumed in forming the coating is similar to that calculated from the anodizing charge, although there may be non-Faradaic contributions to the coating growth.

© 2008 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

Keywords: Titanium; Anodizing; Plasma electrolytic oxidation; Transmission electron microscopy

1. Introduction

Titanium and titanium alloys are used widely for orthopaedic and dental implants due to their biocompatibility. However, the thin, air-formed oxides on the metal surfaces do not form a direct chemical bond with bone tissue, which limits the strength of bonding. Improved bonding has been sought through formation of hydroxyapatite layers on the titanium surface [1], using, for example, plasma spraying [2,3], ion implantation [4,5], biomimetic deposition [6–10] and cathodic electrodeposition [11–14]. There has also been interest in formation of biocompatible anodic films, for instance incorporating calcium and phosphorus [15–22]. Some anodizing processes have been commercialized [19,23,24]. The anodic coatings are usually grown under conditions of dielectric breakdown with sparking on the

titanium surface. The process is often referred to as plasma electrolytic oxidation (PEO), which is used here, or micro-arc oxidation. The growth of coatings under PEO conditions enables modification of oxide properties compared with conventional anodizing below the sparking voltage, such as thickness, chemical composition, crystal structure, porosity, topography and roughness, [25], which have been shown to influence the bone response [26,27]. Sul et al. demonstrated that strong reinforcement of bone tissue reactions occurs with anatase-containing coatings >600 nm thick, with a porous surface morphology [26]. Crystalline oxide also appears to offer reduced corrosion resistance compared with amorphous oxide [28,29]. The structures of anodic films and PEO coatings on titanium are greatly affected by species incorporated into the coating from the electrolyte, with crystallinity being suppressed in coatings-containing silicon, phosphorus and calcium species [29–34].

High-resolution transmission electron microscopy (HRTEM) investigations of PEO coatings are limited and

* Corresponding author. Tel.: +44 161 306 4872.

E-mail address: p.skeldon@manchester.ac.uk (P. Skeldon).

mainly relate to aluminium. Several studies of aluminium agree on the presence of a 100- to 500-nm-thick amorphous layer adjacent to the substrate, followed by a mixture of amorphous and nanocrystalline α -alumina and a nanocrystalline outer layer [35,36]. Further, amorphous silica may form at the coating surface when using a silicate electrolyte [36]. Regarding titanium, conventional anodizing usually involves amorphous-to-crystalline transitions of the anodic titania, as early as ~ 5 V [37]. Nanocrystalline titania is nucleated at the titanium/film interface and oxygen-filled voids subsequently develop within the film above the crystalline oxide [32]. The formation of such gas-filled voids has been shown to precede film breakdown and commencement of sparking at high-voltages [38]. The initial film formed in a commercial alkaline pyrophosphate/aluminate electrolyte under constant current to 80–170 V was shown to consist of an outer layer of amorphous titania and an inner layer-containing anatase, with numerous cavities developed due to the generation of oxygen [39]. A similar anatase structure with internal voids develops in coatings formed in calcium acetate–calcium glycerophosphate based electrolyte for 3 min at 190 V [18].

The present work employs HRTEM to investigate the development of calcium- and phosphorus-containing PEO coatings, with supporting coating analyses. In vitro tests reported elsewhere suggest the potential bioactivity of such types of coating, as assessed by studies of cell proliferation and collagen production using human osteoblast cells [40].

2. Experimental

2.1. Materials

Layers of titanium of 2000 nm thickness were deposited by magnetron sputtering onto 300- μ m-thick electropolished 99.99% aluminium substrates of size 3×2 cm. Electropolishing of the aluminium was carried out in a 4:1 by vol. mixture of ethanol–perchloric acid, at 20 V for 3 min at ~ 5 °C, followed by rinsing in ethanol and deionized water and drying in warm air. The use of a relatively soft aluminium substrate assists the later preparation of electron-transparent sections of coatings using ultramicrotomy. The sputtering was undertaken in an Atom Tech system, with a 99.9% titanium target of 50 mm diameter. The system was first evacuated to 3×10^{-5} Pa, with subsequent deposition of titanium at 320 mA and 345 V in 99.999% argon at 0.5 Pa. The substrates were attached to a copper table, with the temperature remaining below 305 K.

2.2. PEO treatment

Following masking with “stopping-off” lacquer 45 (Canning) to define a working area of 3 cm², specimens were anodized at 2 A m⁻² to 110 V, 190 V and 340 in a mixed (NaPO₃)₆/CaHPO₄ electrolyte prepared from deionized water and high-purity chemicals. The pH was adjusted

to 3.5 with NaOH and H₃PO₄. The coatings were formed with continuous stirring of the electrolyte in a 1 l double-walled glass cell through which a cooled water/glycol mixture was pumped to maintain the electrolyte temperature at 20 °C. A sheet of type 304 stainless steel, of size 7.5×15 cm, was used as the cathode. Voltage responses were recorded electronically, with a sampling time of 20 ms, employing an SCXI data acquisition system (National Instruments) with data analysis by Igor Pro (Wavemetrics). After coating, specimens were rinsed with deionized water and dried in warm air.

2.3. Specimen examination

Electron-transparent sections of coated specimens, nominally 10 nm thick, were prepared by ultramicrotomy and observed by TEM, in a JEOL 2000 FX II instrument operated at 120 kV. Sections were also prepared with a FEI Nova Lab Dual Beam focused ion beam facility and examined by field-emission-gun TEM, using a TECNAI F30 G2 instrument, operated at 300 kV, with a Gatan imaging filter (GIF2001). PEO-treated specimens were examined by scanning electron microscopy (SEM) in an Amray 1810 instrument equipped with energy-dispersive X-ray (EDX) analysis facilities. Phase composition was investigated by X-ray diffraction (XRD), using a Philips XPert-MPD (PW 3040) instrument with a step size of 0.05° and a scan range from 5 to 85° (in 2 θ). Depth profiling analysis of coatings was carried out by glow discharge optical emission spectroscopy (GDOES), employing a Jobin Yvon 5000 RF facility, in an argon plasma of 630 Pa, with RF of 13.56 MHz and power of 35 W. Light emissions were monitored, with a sampling time of 0.01 s, at wavelengths of 130.156, 178.221, 365.350 and 393.367 nm for oxygen, phosphorus, titanium and calcium, respectively. The signals were detected from an area of 4 mm diameter. Coatings were also examined by RBS, using 1.7 MeV He⁺ ions produced by the Van de Graff accelerator of the University of Paris. The ion beam was incident normal to the specimen surface, with scattered ions detected at 165°. The area of analysis was ~ 1 mm². Data were interpreted using the RUMP program.

3. Results

3.1. Voltage–time responses

The voltage–time responses revealed a slow voltage rise for the initial ~ 15 s due to the filling of fine cracks by oxide in the titanium surface (Fig. 1). The cracks arise from internal stress in the deposited titanium. The voltage then rose rapidly at ~ 8.3 V s⁻¹–160 V, followed by a reduced slope, ~ 4.0 V s⁻¹, up to ~ 220 V, with further reductions occurring until the final voltage of 340 V. Apart from the initial region of low slope, the voltage–time response was very similar to that found using bulk titanium substrates. Gas evolution was observed from the first few seconds of anod-

ID	Title	Pages
1538	Transmission electron microscopy of coatings formed by plasma electrolytic oxidation of titanium	11

Download Full-Text Now



<http://fulltext.study/article/1538>



-  **Categorized Journals**
Thousands of scientific journals broken down into different categories to simplify your search
-  **Full-Text Access**
The full-text version of all the articles are available for you to purchase at the lowest price
-  **Free Downloadable Articles**
In each journal some of the articles are available to download for free
-  **Free PDF Preview**
A preview of the first 2 pages of each article is available for you to download for free

<http://FullText.Study>