Anodic Film Growth of Titanium Oxide Using the 3-Electrode Electrochemical Technique: Effects of Oxygen Evolution and Morphological Characterizations

Z. J. Liu,* X. Zhong, J. Walton, and G. E. Thompson*

Corrosion and Protection Centre, School of Materials, The University of Manchester, M13 9PL Manchester, United Kingdom

In the present study, potentiodynamic polarization scans followed by potentiostat anodizing tests have been employed to generate the anodic oxide films on commercially pure Ti in 1 M sulfuric acid and 1 M phosphoric acid. The highly stable single-barrier anodic films with a growth ratio of approximately 1.5 nm V⁻¹ (sulfuric acid) or 1.7 nm V⁻¹ (phosphoric acid) were generated at the anodic voltages from 10 V to 60 V. During the potentiostatic anodizing, the anodic film was formed after the growth of the passive oxide film in the potentiodynamic polarization stage. Oxygen evolution proceeded within both the polarization and the anodizing stages, resulting in the suppression of the current efficiency for the growth of anodic films. The oxygen bubbles were induced by the amorphous-to-crystalline transition within the anodic film, leading to the formation of blister textures. Significant rupture of the anodic film was found that started at 20 V of the anodizing processes in the sulfuric acid; conversely, the significant rupture was started at 50 V in the phosphoric acid. The XRD results indicated that the degree of amorphous-to-crystalline transition in the anodic film formed in the phosphoric acid was less than the film formed in the sulfuric acid. The phosphate titanium oxide layers detected by XPS in the phosphoric acid indicated that more degrees of the amorphous-to-crystalline transition might be inhibited compared with the sulfated titanium oxides found in the sulfuric acid.

© The Author(s) 2015. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.0181603jes] All rights reserved.

Manuscript submitted November 20, 2015; revised manuscript received December 2, 2015. Published December 11, 2015.

Titanium can be anodized in acidic and basic solutions under potentiostatic or galvanostatic conditions. In view of the variation of titanium anodizing conditions, it is possible to tailor the anodic film thickness formed on the surface of titanium.¹ The coloration of the oxide film produced through anodic oxidation is indicative of the thickness. This relation between color and thickness of the oxide is dependent on the anodizing condition and the nature of the electrolyte.² Further, the thickness of the anodic oxide layer has been shown to be a linear function of the applied voltage.²⁻⁵ The anodic oxide film on titanium is basically amorphous in crystal structure and morphologically homogeneous.⁶ Moreover, such an oxide layer provides excellent resistance to corrosion as indicated electrochemically by a low level of electronic conductivity,⁷ thermodynamically great stability⁸ and low ion-formation tendency in aqueous environments.⁹ The growth of the oxide thickness results in systemic changes of the surface topology, particularly in the surface pore configuration,¹⁰ whereas electrolyte derived anion incorporation into oxide films will modify the chemical composition as well as the crystal structure.¹¹⁻¹³ It is generally known that titanium behaves as a typical valve metal for which oxide growth involves field-assisted migration of ions through the films and for the thickness to follow Faraday’s law.¹⁴⁻¹⁶ Further, the growth constant values of the anodic film are variable according to many academics.¹⁷⁻¹⁸ It is reported that anodic oxide films of titanium produced in phosphoric acid and sulfuric acid consist of crystalline anatase and/or rutile phases with the occurrence of oxygen evolution.¹⁹ The morphology of this anodic oxide film is significantly dependent upon the anodic voltage.²⁰ It has been reported that the thickness and morphology of anodic oxide films grown on titanium and Ti₆Al₄V alloy could be controlled by varying the anodizing time and voltage.²¹ The morphology of the anodic film layer could undergo drastic changes as the time of anodizing increased.²¹ It has also been reported that the distribution of the crystalline anodic oxide film formed on titanium can be correlated with the ionic transport during the film growth. The transport number of cations in the amorphous anodic titania is 0.35–0.38.²²⁻²⁴ The outer 35–38% of the film is formed at the film/electrolyte interface through the egress of Ti⁶⁺ ions, with the remaining film formed at the metal film interface by the ingress of O₂/ OH⁻ ions.²⁴ The electrolyte-derived species are mainly incorporated into the outer layer of the anodic films and may stabilize the amorphous structure.²⁵

The traditional anodizing technique employed a lab DC power supply to apply a constant voltage/current directly, and the anodizing is processed for a period of time. The technique can generate an anodic oxide film quickly and directly. Here, a new anodizing method using the classic 3-electrode electrochemical system is proposed. A potentiodynamic polarization test is used to obtain a passive oxide film before the subsequent potentiostatic anodizing, and the passive film is assumed to continuously grow to form the anodic oxide film during the following anodizing procedure. This technique may be useful to generate a compact and stable anodic oxide film which could grow on titanium. Thus, the present paper aims to understand the mechanism of anodic film growth on titanium using this technique.

Experimental

Titanium specimens, of dimensions of 3.0 × 1.5 cm, were fabricated from grade II commercially pure titanium sheet of 1.0 mm thickness. The specimens were masked by lacquer 45 to expose a working electrode area of 1.0 cm². The specimens were successfully wet ground on silicon carbide (SiC) paper from grade 400 to 1200, with subsequent polishing with 2 μm diamond paste and an inorganic lubricant to complete the surface finish. After polishing, the specimens were cleaned in acetone, rinsed in de-ionized water and dried in a cool air stream. The anodizing processes were carried out in 1 M H₂SO₄ and 1 M H₃PO₄ respectively at ambient temperature with continuous mild stirring. A Solartron Modulab System was used and a classic electrochemical 3-electrode cell was employed, comprising a platinum counterelectrode, a saturated calomel reference electrode (SCE) and the titanium working electrode. The schematic diagram of Fig. 1a shows that the potentiodynamic polarization was undertaken at a scan rate of 100 mV s⁻¹ in order to reach the selected anodic voltage, thereby quickly creating a passive oxide film. Then, the anodic voltage was continuously applied constantly to grow the anodic film, and the current-time response during anodizing was recorded by the Modulab ECS software (Fig. 1b).

Following the anodizing procedures, the titanium specimens were cleaned by de-ionized water, dried in a cool air stream and stored in a desiccator for future analysis. The morphologies of the anodic oxide films were examined by scanning electron microscopy (SEM)
using a Zeiss Ultra 55 instrument with an acceleration voltage of 5 kV. Selected cross-sections of anodic films were evaluated by transmission electron microscopy (TEM), using a Tecnai F30 instrument at an acceleration voltage of 300 kV. Prior to the TEM observations, the specimens were milled with a focused-ion beam (FIB), using a FEI Quanta 3D FEG facility. A thin platinum layer was coated on the film for the protection purpose before the fabrication of FIB.

The crystalline structures of anodic oxide films were examined by X-ray diffraction (XRD), using a Philips X’pert Modular Powder Diffractometer and a long fine focus copper anode X-ray source. The scanning range (2θ) from 10° to 85° was conducted. The contents of the anodic oxide films were qualitatively compared by the height of crystal structure and semi-quantitatively calculated by summing up the integrated intensity of the main peaks of anatase. The resultant peaks were fitted and analyzed by the X’Pert HighScore Plus software.

The chemical compositions of the anodic oxide films and the valence states of titanium, oxygen, sulfur, phosphorus and carbon species were determined by X-ray photoelectron spectroscopy (XPS), using a Kratos Axis Ultra spectrometer with a monochromatic Al Kα source (15 mA, 14 kV). High resolution spectra were charge-compensated by setting the binding energy of the C1s peak to 284.0 eV. The XPS software were analyzed by the CasaXPS software.

The dielectric properties of the anodic oxide films were examined by electrochemical impedance spectroscopy, which was carried out in a potentiostatic mode vs. the open circuit potential. A voltage perturbation amplitude of 10 mV with 10 points per decade without start delay was set up. The testing frequency was scanned from 100 kHz to 1 Hz, where the capacitive effects of the anodic oxide films dominated.

Results and Discussion

Potentiodynamic polarizations, current – time responses and colorations.—Fig. 2a shows a potentiodynamic polarization regime from 0 V (vs. SCE) to 60 V (vs. SCE) in the sulfuric acid and phosphoric acid respectively. Both polarization curves show that the currents required for the passive oxide growth are initiated from ~1 V to ~6 V, and the current densities are increased significantly due to the occurrence of oxygen evolution between ~6 V and ~13 V. From ~13 V to ~60 V, the currents are spent for the growth of passive oxide films and oxygen evolution. The rising tendency of the current densities is reduced due to the growth of passive oxide films. Interestingly, the current density in the phosphoric acid from the potential of ~13 V to 60 V is slightly decreased, and within the potential region it is lower than the current density in the sulfuric acid. Further, the current density from ~13 V to 60 V in the sulfuric acid still increased slightly. The potentiodynamic polarization results indicate that the currents are mainly responsible for the growth of the passive oxide film and oxygen evolution. The anodic film would be formed during the further potentiostatic anodizing based on the passive oxide film generated during the previous polarization.

Fig. 2b shows the current-time responses during the anodizing in the sulfuric acid. It is revealed that the current densities decrease rapidly at the commencement of ~50 s, and the decrease is reduced gradually from ~50 s to 900 s. The current densities from the anodic voltages of 10 V to 60 V after 900 s are listed in Table I, showing that the current densities increase gradually with the increase of anodic voltage. Fig. 2c reveals that the current densities during anodizing in the phosphoric acid similarly decrease sharply at the beginning of ~50 s, and drop slowly within the next 850 s. Table I lists the relative current densities during anodizing in the phosphoric acid, indicating that the current density also increases as the anodic voltage increases. The cell charges spent for the growth of the films are determined by Faraday’s law; therefore, the charge values can be calculated based on the equation of \( Q_t = \frac{I_t \times t}{n \times F} \) where \( Q_t \) is the charge (C) and \( t \) is anodizing time (s). As a result, the charges are estimated in the values from 0.08 C cm\(^{-2}\) to 0.29 C cm\(^{-2}\) (sulfuric acid) and from 0.10 C cm\(^{-2}\) to 0.58 C cm\(^{-2}\) (phosphoric acid) at the voltages from 10 V to 60 V. The oxygen evolution was confirmed by the visible oxygen bubbles on the titanium surface during the anodizing stages.

Figure 3 shows the colorations of the specimen surfaces after the anodizing procedures due to the interference effect. Depending on the anodic voltages, the surface follows a chromatic scale and varies from golden to dark yellow violet color after anodizing at voltages between 10 V and 60 V in the sulfuric acid. For the phosphoric acid, dark golden to pale yellow color are displayed after anodizing from 10 V to 60 V.

Scanning and transmission electron microscopies.—Figure 4 shows the scanning electron micrographs of the anodic films formed by anodizing at voltages from 10 V to 60 V in the sulfuric and phosphoric acids. A compact anodic film structure is formed at 10 V in the sulfuric acid (Fig. 4a). The anodic film ruptures at some of the local regions after anodizing at 20 V (Fig. 4b). The anodic film blisters are formed due to the bursting of oxygen bubbles within the film formed at 30 V (Fig. 4c). The ruptures of the films induce nanocracks, which are evident after anodizing at 40 V and 50 V (Figs. 4d and 4e). Further, similar blister induced cracks are observed following the anodizing stages at 60 V (Fig. 4f). In accordance with the anodizing in the phosphoric acid, anodic films with small blisters developed within different regions are observed at 10 V, 20 V and 30 V (Figs. 5a, 5b and 5c). The blisters are structured in larger sizes at 40 V compared with 10 V, 20 V and 30 V (Fig. 5d). While at 50 V, the ruptures of the film are initiated within the blisters due to the bursting of oxygen bubbles (Fig. 5e). At 60 V, a similar film texture
Figure 3. The colorations of anodic film surfaces formed after the anodizing stages in sulfuric acid (upper images) and phosphoric acid (lower images) at anodic voltages between 10 V and 60 V.

Figure 2. (a) Potentiodynamic polarization curves scanning from 0 V (vs. SCE) to 60 V (vs. SCE) in sulfuric acid and phosphoric acid respectively. (b) Current-time responses at different anodic voltages between 10 V and 60 V in sulfuric acid. (c) Current-time responses at different anodic voltages between 10 V and 60 V in phosphoric acid.

Table I. Current densities (A cm$^{-2}$) after anodizing cp-Ti at anodic voltages from 10 V to 60 V for 900 s in 1 M sulfuric acid and 1 M phosphoric acid.

| Anodizing Current Density (A cm$^{-2}$) | 10 V  | 20 V  | 30 V  | 40 V  | 50 V  | 60 V  |
|----------------------------------------|------|------|------|------|------|------|
| H$_2$SO$_4$                            | 9.0 $\times$ 10$^{-5}$ | 1.6 $\times$ 10$^{-4}$ | 1.8 $\times$ 10$^{-4}$ | 2.0 $\times$ 10$^{-4}$ | 2.1 $\times$ 10$^{-4}$ | 3.2 $\times$ 10$^{-4}$ |
| H$_3$PO$_4$                            | 1.1 $\times$ 10$^{-4}$ | 1.5 $\times$ 10$^{-4}$ | 1.6 $\times$ 10$^{-4}$ | 3.5 $\times$ 10$^{-4}$ | 5.8 $\times$ 10$^{-4}$ | 6.4 $\times$ 10$^{-4}$ |

is shown compared with 50 V (Fig. 5f). Further, the microstructures reveal that the ruptures of the anodic film are initiated in the sulfuric acid at a lower anodic voltage (20 V) than the voltage (50 V) after anodizing in the phosphoric acid. Additionally, the scanning electron micrographs shown in Fig. 4 indicate that at a higher anodic voltage, the potentiodynamic polarization is applied first to form a passive oxide film, ranging from 0 V (vs. SCE) to the selected anodic voltage (vs. SCE) with the occurrence of oxygen evolution. Consequently, the oxygen bubbles and oxygen-filled cavities may be induced within the pre-formed passive oxide film prior to the potentiostatic anodizing.

The cross-sections of anodic films formed at 50 V in the two acids respectively are shown in the transmission electron micrographs of Figure 6. For anodizing in the sulfuric acid (Fig. 6a), an anodic film of $\sim$75 nm thickness is formed, which is consistent with the thickness-to-voltage ratio of $\sim$1.5 nm V$^{-1}$. The lattice fringes observed in Fig. 6b indicate that the amorphous-to-crystalline transition occurred during the film growth by anodizing. At the higher magnification (Fig. 6c), lattice fringes within the film with spacings of 3.5 Å and 1.7 Å are revealed, and the (101) and (004) crystal planes correspond to the spacings. Further, nanoscale bubbles have developed around the nanocrystals, resulting in the generation of oxygen-filled voids, as indicated by the arrow in Fig. 6c. For anodizing in the phosphoric acid, an anodic film thickness of $\sim$85 nm is generated (Fig. 6d), which corresponds to the thickness-to-voltage ratio of $\sim$1.7 nm V$^{-1}$. The crystalline phases are observed within different regions of the film and the regions near the interface Ti/TiO$_2$ (Fig. 6e). At the higher magnification (Fig. 6f), lattice fringes are clearly observed within the film, and the crystal planes of (101) and (002) corresponding to the spacings of 3.5 Å and 1.6 Å are determined (Fig. 6f). As evident from the transmission electron micrographs in Figure 6, the suppression of the current efficiency responsible for the anodic film growth is triggered by the amorphous-to-crystalline transition. The resultant crystalline phases introduce a high electron-conducting passage for the development of oxygen bubbles.

X-ray diffraction and X-ray photoelectron spectroscopy.— Different anatase peaks, including (101), (200), (105) and (224) through the angles from 10$^\circ$ to 85$^\circ$ are shown in the X-ray diffraction patterns of the titanium anodized at 50 V in the sulfuric acid (Fig. 7a). Conversely, the anodic films formed after anodizing at 30 V and 10 V show titanium peaks mostly, indicating that less anatase crystalline phases are developed within the films compared with the film formed at 50 V. In the phosphoric acid, only one peak corresponding to the (224) crystal plane of anatase is detected for the anodic films formed after anodizing at 10 V, 30 V and 50 V (Fig. 7b). According to the crystalline performance of the X-ray diffraction patterns, a certain...
The degree of the amorphous-to-crystalline transition during the growth of anodic film may be impeded by the incorporation of phosphate anions, which are particularly evident by the films formed at 50 V in both acids respectively.

Figure 8 shows the X-ray photoelectron spectra of anodic films formed after anodizing at 50 V in both acids. Fig. 8a displays the high resolution Ti2p peaks of the films formed in both acids. A characteristic Ti2p doublet structure corresponding to the peaks at 454.7 eV and 461.1 eV is identified, and the peaks are attributed to Ti4+. The high resolution O1s spectra shown in Fig. 8b are disclosed at 530.2 eV, 531.8 eV and 533.0 eV. The peaks could be deconvoluted to 530.1 eV, 531.2 eV and 533.0 eV for Ti-O bonds, Ti-OH bonds, and adsorbed water (H2O). The evident O1s spectra indicate that hydroxide, hydroxyl groups, bound water, and hygroscopic water are produced. Further, the distribution of the crystalline oxide can be correlated with an ionic transport. In general, the crystalline phase has a higher ionic resistivity, and hence a higher electric field than the amorphous phase. Thus, the probability of excitation of electrons in the valence band, formed by overlapping of O2p orbitals in the crystalline titania, and the conduction band is enhanced, leading to the oxidation of O2 ions to form O2 molecules and gas bubbles. Finally, the oxygen-filled cavities in the anodic film are developed. The increased pressure in the oxygen bubbles within the film results in the formation of blisters, and the rupture of the film is induced eventually by bursting of the bubbles.

Moreover, in Fig. 8c, the carbon species responding to a major peak at 282.8 eV and two peaks at 286.6 and 289.9 eV are revealed. The peaks are assigned to C-C/C-H (284.8 eV), C-O (286.7 eV) and O-C=O (288.9 eV) groups. The high resolution spectrum of the C1s peaks features a small amount of carbonaceous species within the anodic films formed in both acids. The presence of carbon species was probably produced from surface contamination during sample handling or material machining. Additionally, a small amount of carbon species detected by XPS comprise hydrocarbon species with small
amounts of singly and doubly bound oxygen. Therefore, the hydrocarbon species could be of interest as an inhibitor that hinders oxygen evolution by adsorbing a certain amount of oxygen through carbon species, which optimizes the current efficiency for anodic film growth. However, this inhibition mechanism is still not clear until further studies are conducted.

The XPS resolution spectrum of S2p detected at ~169.2 eV from anodizing in the sulfuric acid indicates the presence of sulfated titanium oxides (TiSO₄ and Ti₂(SO₄)₃) are probably generated (Fig. 8d). It is also implied that in the sulfuric acid, the anodic film could be dissolved as Ti²⁺ and Ti³⁺ ions into the electrolyte. For the phosphoric acid, the XPS spectrum of P2p measured at ~133.4 eV indicates that the phosphate titanium oxides (TiPO₄ and Ti₃(PO₄)₂) are probably formed (Fig. 8e). These phosphate oxide film layers formed on the anodic film surface may inhibit more degrees of amorphousand crystalline transition compared with the sulfated titanium oxide layers. However, it is still not fully clear that how much more the amorphous-to-crystallization transition could be inhibited by the phosphate titanium oxides compared with the sulfated titanium oxide until the future work is carried out.

**Electrochemical impedance spectroscopy.**—The Bode diagrams of the anodic films formed in the sulfuric and phosphoric acids at the voltages from 10 V to 60 V are displayed in Figure 9. The impedance spectra as a function of the anodic voltages are presented in Figs. 9a and 9b. Over the frequency range inspected, the impedance increases significantly with the increase of anodic voltage, suggesting that the capacitance of the anodic film is reduced from 10 V to 60 V. Further, one time constant is observed since the impedance changes approximately linearly at a slope of ~−1 with frequency. Moreover, the relationship between the capacitance and the anodic voltage is shown in Figs. 9c and 9d. A predominantly capacitive behavior is evident from the medium to the low frequency as the phase angle is approaching −90°. It indicates that highly stable anodic films are formed on titanium during anodizing in both acids. The one time constants are also confirmed by the Nyquist diagrams which are shown in Figs. 9e and 9f. The Nyquist plots disclose that the single anodic barrier-layer films are formed on the titanium.

The results were fitted by an equivalent circuit consisting of a capacitor, accounting for the capacitive behavior of the anodic film, in parallel with a resistor for the dissipative resistance to the current density spent for the growth of anodic film, both in series with a resistor responsible for the solution resistance. The capacitance data were used to obtain a qualitative estimation of the dielectric permittivities of the anodic films after anodizing in the two acids. According to the calculation by \[ \varepsilon = \frac{\varepsilon_0 \varepsilon_r}{T} \] where \( T \) is the anodic film thickness (nm), \( \varepsilon \) is the dielectric permittivity of TiO₂ formed in each acid, \( \varepsilon_0 \) is the dielectric permittivity of free space (8.85 \times 10⁻¹² F m⁻¹) and \( \varepsilon_r \) is the oxide capacitance (F cm⁻²) and the real film thickness measured by TEM, the dielectric permittivities of the anodic films formed after anodizing at 50 V in the sulfuric acid and phosphoric acid at ambient temperature.
Figure 8. High resolution XPS spectra of (a) Ti2p peak, (b) O1s peak and (c) C1s peak within the anodic films formed after anodizing at 50 V in the sulfuric and phosphoric acids; (d) S2p peak of the film formed in sulfuric acid, and (e) P2p peak of the film formed in phosphoric acid.

shows that it is dependent upon the nature of electrolyte. The value of permittivity of the anodic film formed in the sulfuric acid is higher than the film formed in the phosphoric acid. It is inferred that the electron conductivity of the anodic oxide film generated in the sulfuric acid is higher. On the other hand, as the dielectric permittivity has been determined, the relationship between the anodic film thickness and the anodic voltage can be estimated as shown in Figure 10. As expected, the relationship between the anodic film thickness and the anodic voltage shows a good agreement with a linear function. Further, it shows that the anodic film thickness formed in phosphoric acid is larger than the film thickness formed in sulfuric acid at each of the anodic voltages.
Conclusions

1) Highly stable single-barrier anodic films could be formed using the classic 3-electrode electrochemical technique. In the technique, a potentiodynamic polarization was applied from 0 V (vs. SCE) to selected anodic voltages between 10 V and 60 V (vs. SCE), which was followed by the potentiostatic anodizing at the selected anodic voltage in 1 M sulfuric acid or 1 M phosphoric acid.

2) The amorphous-to-crystalline transition occurred during the growth of anodic films in the sulfuric acid and the phosphoric acid. Oxygen evolution developed in the potentiodynamic polarization which was also induced in the following potentiostatic anodizing process, resulting in the formation of the blister textures in the anodic films. The ruptures of anodic films were initiated within the blisters formed by bursting of oxygen bubbles. The rupture of the anodic film formed was started at the anodic voltage of 20 V during anodizing in the sulfuric acid but at 50 V in the phosphoric acid.

3) Phosphate anions incorporated into the anodic films formed in the phosphoric acid may inhibit a certain degree of the amorphous-to-crystalline transition during the anodizing, resulting in the development of a reduced extent of crystallinity within the films compared with the films formed in the sulfuric acid.

Acknowledgments

The authors are grateful to the Engineering and Physical Sciences Research Council (UK) for support of the LATEST2 Programme grant (EP/H020047/1).
Figure 10. Anodic oxide film thicknesses generated after anodizing at each of anodic voltage in sulfuric acid and phosphoric acid respectively. The relationship between the anodic film thicknesses and the anodic voltages in either sulfuric acid or phosphoric acid shows a linear function.

References

1. J.-L. Delplancke, A. Garnier, Y. Massiani, and R. Winand, “Influence of the anodizing procedure on the structure and the properties of titanium oxide films and its effect on copper nucleation,” Electrochimica Acta, 39, 1281 (1994).
2. Y.-T. Sul, C.B. Johansson, Y. Jeong, and T. Albreksson, “The electrochemical oxide growth behavior on titanium in acid and alkaline electrolytes,” Medical Engineering & Physics, 23, 329 (2001).
3. L. Jukka, K. Bengt, M. Hakan, and O. Hans, “Multi-technique surface characterization of oxide films on electropolished and anodically oxidized titanium,” Applied Surface Science, 45, 189 (1990).
4. M. Schneider, S. Schroth, J. Schilm, and A. Michaelis, “Micro-EIS of anodic thin oxide films on titanium for capacitor applications,” Electrochimica Acta, 54, 2663 (2009).
5. A. Yildiz, N. Serin, M. Kasap, T. Serin, and D. Mardare, “The thickness effect on the electrical conduction mechanism in titanium oxide thin films,” Journal of Alloys and Compounds, 493, 227 (2010).
6. G. Radegran, J. Laussmaa, L. Mattsson, U. Rolander, and B. Kasemo, “Preparation of ultra-thin oxide windows on titanium for tem analysis,” Journal of Electron Microscopy Technique, 19, 99 (1991).
7. H. Zitter and H. Plenk Jr., “The electrochemical behavior of metallic implant materials as an indicator of their biocompatibility,” Journal of Biomedical Materials Research, 21, 851 (1987).
8. R. J. Solar, S.R. Pollack, and E. Korostoff, “In vitro corrosion testing of titanium surgical implant alloys: An approach to understanding titanium release from implants,” Journal of Biomedical Materials Research, 13, 217 (1979).
9. P. Tengvall and I. Lundstrom, “Physico-chemical considerations of titanium as a biomaterial,” Clinical Materials, 9, 115 (1992).
10. Y.-T. Sul, C.B. Johansson, S. Petronis, A. Krozer, Y. Jeong, A. Wennerberg, and T. Albreksson, “Characteristics of the surface oxides on turned and electrochemically oxidized pure titanium implants up to dielectric breakdown: the oxide thickness, micropore configurations, surface roughness, crystal structure and chemical composition,” Biomaterials, 23, 491 (2002).
11. Lj. D. Arsov, C. Kormann, and W. Pleth, “Electrochemical synthesis and in situ Raman spectroscopy of thin films of titanium dioxide,” Journal of Raman Spectroscopy, 22, 573 (1991).
12. G. Bloudeau, M. Froischer, M. Froment, and A. Hugot-Le-Goff, “Structure and growth of anodic oxide films on titanium and Ta6V alloy,” Journal of the Less Common Metals, 56, 215 (1977).
13. da. F. Carlos, T. Angnes, T. Abderrahmane, and da. C. B. Manuel, “A characterization of titanium anodic oxides by X-ray absorption spectroscopy and grazing X-ray diffraction,” Journal of Electroanalytical Chemistry, 388, 115 (1995).
14. J. Yahalom and J. Zahavi, “Electrolytic breakdown crystallization of anodic oxide films on Al, Ta and Ti,” Electrochimica Acta, 15, 1429 (1970).
15. Y.-T. Sul, and I. Kamal, “Kinetics of anodic oxide-film growth on titanium—I. Acid media,” Electrochimica Acta, 16, 1539 (1971).
16. L. Jukka, K. Bengt, M. Hakan, and O. Hans, “Multi-technique surface characterization of oxide films on electropolished and anodically oxidized titanium,” Applied Surface Science, 45, 189 (1990).
17. L. Jukka, K. Bengt, M. Hakan, and O. Hans, “Multi-technique surface characterization of oxide films on electropolished and anodically oxidized titanium,” Applied Surface Science, 45, 189 (1990).
18. M. Schneider, S. Schroth, J. Schilm, and A. Michaelis, “Micro-EIS of anodic thin oxide films on titanium for capacitor applications,” Electrochimica Acta, 54, 2663 (2009).
19. A. Yildiz, N. Serin, M. Kasap, T. Serin, and D. Mardare, “The thickness effect on the electrical conduction mechanism in titanium oxide thin films,” Journal of Alloys and Compounds, 493, 227 (2010).
20. G. Radegran, J. Laussmaa, L. Mattsson, U. Rolander, and B. Kasemo, “Preparation of ultra-thin oxide windows on titanium for tem analysis,” Journal of Electron Microscopy Technique, 19, 99 (1991).
21. H. Zitter and H. Plenk Jr., “The electrochemical behavior of metallic implant materials as an indicator of their biocompatibility,” Journal of Biomedical Materials Research, 21, 851 (1987).
22. R. J. Solar, S.R. Pollack, and E. Korostoff, “In vitro corrosion testing of titanium surgical implant alloys: An approach to understanding titanium release from implants,” Journal of Biomedical Materials Research, 13, 217 (1979).
23. P. Tengvall and I. Lundstrom, “Physico-chemical considerations of titanium as a biomaterial,” Clinical Materials, 9, 115 (1992).
24. Y.-T. Sul, C.B. Johansson, S. Petronis, A. Krozer, Y. Jeong, A. Wennerberg, and T. Albreksson, “Characteristics of the surface oxides on turned and electrochemically oxidized pure titanium implants up to dielectric breakdown: the oxide thickness, micropore configurations, surface roughness, crystal structure and chemical composition,” Biomaterials, 23, 491 (2002).