# Characterization of the Growth of Titania Coatings Under Plasma Electrolytic Oxidation of Titanium

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Plasma electrolytic oxidation (PEO) can be successfully used to enhance the surface properties of titanium, such as corrosion resistance, tribological performance, and biocompatibility, for practical application in aerospace and biomedical areas. However, understanding of the mechanisms of coating growth, necessary for regulation of the PEO processes and tailoring of surface characteristics, remains insufficiently clear. Coating formation on chemically-polished titanium is considered here under galvanostatic and potentiostatic conditions of PEO in phosphate electrolytes, with the structure, composition, and morphology of the coatings investigated by SEM, AFM, EPMA and XRD. Further, incorporation of foreign ions, through sequential anodizing, is used to identify the transport paths of species within the coating and to determine the sites of coating growth. Coatings consist mainly of amorphous titania, anatase and rutile, with the last increasing with increased current density. The efficiency of coating growth decreases with time of treatment, and also with increase of current density, falling below 10% after 20 min of coating at current densities in the range 20 to 100 mA cm<sup>-2</sup>. Phosphorus and, in the case of sequential anodizing, tungsten species are incorporated into the coating, the latter being found in most regions of the coating, indicating the role of short-circuit transport processes in coating growth. The initial breakdown of the coating is shown to occur at relatively low voltages, without sparking, with certain grains with residual nanotextures from chemical polishing being preferred sites.

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## **1.Introduction**

The application of anodic titania coatings in aerospace, gas and oil, electrical engineering and electronics, chemical and biomedical industries utilizes their various properties, including corrosion resistance, anti-fretting, anti-galling and wear-resistance, heat-resistance, optical, semiconductive, piezoelectric, ferroelectric and optoelectric, and biocompatibility. Plasma electrolytic oxidation (PEO), also called anodic spark deposition (ASD) or micro-arc oxidation  $(MAO)^{1, 2}$  and anodic oxidation under spark discharge  $(ANOF)^{3, 4}$ , is of increasing interest as a coating process. PEO is based on the modification of a growing anodic oxide by spark/arc microdischarges, which are initiated at potentials above the breakdown voltage of the oxide<sup>5</sup>. The coating mechanism is considered to involve variously anodizing of the substrate, diffusion deposition, electrophoretic deposition, and thermal ionization and condensation. High local temperature  $(10^3 - 10^4 \text{ K})$  and pressure  $(10^2 - 10^3 \text{ MPa})$  inside the discharge channel assist plasma thermochemical interactions, resulting in ceramic coatings, that incorporate substrate and electrolyte species, with properties differing from those of anodic oxides produced by other routes. Dielectric breakdown during conventional anodizing may include electron injection into the oxide, followed by avalanching and current runaway, and Joule heating at fissures and flaws in the film<sup>6, 7</sup>, with film defects being preferred breakdown sites<sup>8</sup>. Mechanistic models of microarc discharge include heat-induced dielectric breakdown<sup>9</sup>, partial gas cathodes with gas envelope formation near the anode surface<sup>3, 10</sup>, and electron avalanches<sup>11</sup>.

The present work examines PEO coatings formed on titanium in phosphate electrolytes, with focus on the relation of thickness, morphology, structure and composition of coatings to current and charge densities. Additionally, tungsten species are used as a tracer to identify transport paths of reactants and sites of coating growth.

## 2. Experimental

## Materials

Specimens of thermally-annealed, 1 mm (0.04 in.) thick, titanium foil, (ADVENT Research Materials Ltd., England: 3000 ppm Fe, 750 ppm O, 55 ppm N, <800 ppm C), of working area 3 cm<sup>2</sup> (1.2 in<sup>2</sup>) were employed. Prior to anodizing the specimens were degreased in acetone and ethanol, rinsed in deionised water and subsequently polished in a mixture of 48%HF and 70%HNO<sub>3</sub> (1:3 by vol.) for 1 min. The specimens were then rinsed with deionised water and dried in warm air. Specimens were weighed before and after anodizing.

## Plasma electrolytic oxidation

Galvanostatic and potentiostatic anodizing was carried out using a regulated DC power supply, Metronix 410A-500, in a double-walled glass beaker, with control of temperature at 20°C (68°F) by an external thermostat. Stainless steel was employed as a cathode. All electrolytes were prepared from deionized water and high-purity chemicals supplied by Fisher Scientific U.K. The electrolytes (Table 1) were stirred with a magnetic stirrer and allowed to equilibrate for 24 h at room temperature. The PEO conditions are given in Tables 2 and 3, voltage-time responses were recorded on a flatbed recorder. After coating, specimens were rinsed with deionised water and dried in warm air. Thickness measurements were made for each coatings using an eddy current meter (FISHERSCOPE® PERMASCOPE) with the average of ten measurements cited.

## Inductively coupled plasma optical emission spectroscopy (ICP-OES)

The concentration of dissolved titanium ions was measured with an inductively coupled optical emission axial spectrophotometer (VARIAN Vista MPX) at three emission wavelengths of 334.941, 336.122 and 337.280 nm, with a power of 1 kW, plasma flow of 15 L/min (0.26 gal/min) and replica read time of 15 s. Calibration employed 5 and 50 ppm solutions prepared from a certified 1000 ppm solution. For each measurement, 15 mL specimens were nebulized through a concentric nozzle, with argon as a carrier gas, at a flow rate of 0.8 mL/min (0.2 mgal/min). Three analyses were carried out for each electrolyte.

## Specimen examination

The surface of chemically polished titanium was examined in air by atomic force microscopy (AFM), employing a Nanoscope instrument (Veeco) in the tapping mode. Scanning electron microscopy (SEM), was used for examination of the morphology and composition of coated specimens. Sufficiently thick coatings were investigated X-ray diffraction, using a Philips X'Pert – APD (PW 3710) X-ray diffractometer, with Cu Ka radiation, at a scanning speed of  $0.008^{\circ}$ /sec and a scan range from 5 to  $85^{\circ}$  (in  $2\theta$ ). The X-ray generator settings were 50 kV and 40 mA. The structure of relatively thin coatings was examined with a Philips X'Pert – MPD (PW 3040) instrument with a step size  $0.005^{\circ}$  and a scan range from 5 to  $85^{\circ}$  (in  $2\theta$ ). Elemental distributions in coatings were determined by electron probe micro analysis (EPMA) using a CAMECA SX-100 instrument at an accelerating voltage of 15 kV with a beam current of 200 nA in mapping mode and 20 nA in backscattered electron imaging mode. Cross-sections of coatings were prepared by grinding through successive grades of SiC, followed by diamond finishing to 1  $\mu$ m (40  $\mu$ in.)

## 3. Results

## 3.1. Voltage-time response

Galvanostatic anodizing, at 20 mA/cm<sup>2</sup> (125 mA/in<sup>2</sup>), in the phosphate electrolytes resulted in highly reproducible voltage-time behaviour (Fig. 1, Table 1). From the commencement of anodizing, the voltage increased approximately linearly with time to ~160 V at 6.53 V s<sup>-1</sup> for both electrolytes. Subsequently reduced slopes of approximately 2.19 V s<sup>-1</sup> to ~260 V, 0.73 V s<sup>-1</sup> to 350 V, 0.40 V s<sup>-1</sup> to 400 V, and 0.22 V s<sup>-1</sup> to 440 V were revealed, the last was the final voltage for anodizing in the 0.026 M electrolyte. Similarly, slopes of approximately 1.71 V s<sup>-1</sup> to ~250 V, 0.92 V s<sup>-1</sup> to 300 V and 0.26 V s<sup>-1</sup> to 350 V, the final voltage, were determined for anodizing in the 0.052M electrolyte. The coating produced in the 0.026 M electrolyte was of uniform matt gray appearance, whereas that formed in the 0.052 M electrolyte revealed also darker tracks from persistent, traveling sparks. For anodizing in 0.026 M Na<sub>3</sub>PO<sub>4</sub> electrolyte, the rate of voltage rise increases with increase of current density (Fig. 2). Gradual reduction of the slope is observed for each current density up to the final anodizing voltages, which increased slightly with increase of current density (Fig. 3, Table 2). The reduction of the slopes of the voltage-time curves with time is in agreement with earlier work<sup>12</sup>, where it was

suggested to result from increased conductance of the coating and decreased current efficiency of film formation.



Fig.1. Voltage-time responses for anodizing of titanium at 20 mA/cm<sup>2</sup> (125 mA/in<sup>2</sup>) in different Na<sub>3</sub>PO<sub>4</sub> electrolytes at 20°C ( $68^{\circ}F$ ).



Fig.2. Voltage-time responses for anodizing of titanium at different constant current density in 0.026 M Na<sub>3</sub>PO<sub>4</sub> at 20°C ( $68^{\circ}F$ ).



Fig.3. Dependence of final forming voltage on current density for anodizing of titanium in 0.026 M Na<sub>3</sub>PO<sub>4</sub> electrolyte at 20°C ( $68^{\circ}F$ ) for 20 min.

Table 1. PEO electrolytes						
Composition	pН	Conductivity (mS)				
0.026 M Na <sub>3</sub> PO <sub>4</sub>	12.06	7.95				
0.052 M Na <sub>3</sub> PO <sub>4</sub>	12.17	13.55				
0.1 M Na <sub>2</sub> WO <sub>4</sub>	9.49	15.50				

Table 2. Conditions of galvanostatic anodizing of titanium at 20 mA/cm<sup>2</sup> at 20°C (68°F).

Electrolyte/	Weight	<b>T!</b>	Charge	Coating	Forming	<b>Current efficiency</b>	
(Sparking change change (min)	density (C/cm <sup>2</sup> )	thickness (µm)	rate (nm/s)	(nm <sup>·</sup> cm <sup>2</sup> /C)	η (%)		
0.052 M Na <sub>3</sub> PO <sub>4</sub> (220 V)	-1.82	10	12	3.46	5.76	288.3	53.7
	-1.52	20	24	5.12	4.26	213.3	39.8
	-3.81	30	36	5.92	3.28	164.4	30.7
	-4.81	40	48	6.01	2.5	125.2	23.3
	-7.14	60	72	6.55	1.81	91	16.9
0.026 M Na3PO4 (290 V)	0	10	12	4.00	6.66	333.3	62.2
	0.80	20	24	5.84	4.86	243.3	45.4
	-0.29	30	36	6.67	3.7	185.3	34.5
	0.52	40	48	7.37	3.07	153.5	28.6
	0	60	72	8.21	2.28	114	21.3

at different current densities in 0.026 M phosphate electrolyte at 20°C (68 F).									
Current	Charge	Sparking	Forming	Coating	Forming	Current eff	t efficiency		
density (mA/cm <sup>2</sup> )	density (C/cm <sup>2</sup> )	voltage (V)	voltage (V)	thickness (µm)	rate (nm/s)	nm cm <sup>2</sup> /C	η (%)		
20	24	220	445	5.84	4.86	243.3	45.3		
40	48	220	450	6.93	5.77	144.4	26.9		
60	72	220	460	7.24	6.03	100.6	18.7		
100	120	220	461	8.71	7.25	72.6	14.1		
150	180	220	462	8.53	7.1	47.4	9.2		

Table 3. Conditions of galvanostatic anodizing of titanium for 20 min t different current densities in 0.026 M phosphate electrolyte at 20°C (68°F)

# 3.2. Coating thickness measurements

Coatings thickened with increase of charge density for both electrolytes (Fig. 4). However, the average formation rates, determined from the coating thickness and total time of anodizing, decreased from 5.76 nm/s to 1.81 nm/s in 0.052 M electrolyte, and from 6.66 to 2.28 nm/sec in 0.026 M electrolyte for treatment time between 10 to 60 min (Table 2). For treatments of 20 min, coatings thickness increased with increase of current density to 100 mA/cm<sup>2</sup> (625 mA/in<sup>2</sup>) (Fig. 5), but changed little from 100 to 150 mA/cm<sup>2</sup> (938 mA/in<sup>2</sup>).



Fig.4. Dependence of coating thickness on charge density for anodizing of titanium at 20 mA/cm<sup>2</sup> (125 mA/in<sup>2</sup>) in Na<sub>3</sub>PO<sub>4</sub> electrolytes at 20°C (68°F).



Fig. 5. Dependence of coating thickness on current density for anodizing of titanium in 0.026 M Na<sub>3</sub>PO<sub>4</sub> at 20  $\degree$  (68°F) for 20 min.

### 3.3. Weight measurements and anodic dissolution.

Relatively large weight losses occurred after anodizing in 0.052 M electrolyte, whereas the weight remained approximately almost constant during anodizing in 0.026 M electrolyte (Fig. 6). For the former electrolyte, the amount of dissolved titanium was approximately 10 times lower than the recorded weight losses (Fig. 7).



*Fig.6. Variation of the specimen weight change on charge density for anodizing of titanium at 20 mA/cm<sup>2</sup> (125 mA/in<sup>2</sup>) in 0.052 M Na*<sub>3</sub>*PO*<sub>4</sub> *electrolyte at 20°C (68°F).* 



Fig.7. Variation of dissolved titanium in solution on the charge density for anodizing of titanium at 20 mA/cm<sup>2</sup> (125 mA/in<sup>2</sup>) in 0.052 M Na<sub>3</sub>PO<sub>4</sub> electrolyte at 20°C (68°F).

3.4. Structure and morphology of oxide films.

#### 3.4.1. Atomic force microscopy

Atomic force microscopy images of chemically polished titanium, with a grain size 10 - 50  $\mu$ m (0.4 – 2 mil), revealed differing rates of etching of individual grains (Fig. 8). Nanotextured grains, with slower polishing rate, protruded above the surrounding smoother grains, by about 200 nm (Fig. 9). The arithmetic mean roughness, Ra, the root mean square deviation, Rq, and the maximum height of the profile within a sample length, Rz, for area A of a protruding nanotextured grain were 121, 148 and 812 nm, respectfully; compared with 3 nm, 5 nm, 134 nm for area B of a an adjacent smoother grain (Fig. 8).



Fig.8. AFM image of chemically polished titanium: (a) tapping mode scan; (b) 3-D topography.



Fig.9. Height profile of chemically polished titanium along the line indicated in Fig.8(a).

# 3.4.2. Scanning electron microscopy

An influence of the substrate grains was evident on anodizing after film formation at 50 and 150 V for 15 min, with uniform film formation on the relatively smoother grains (Fig. 10 a, b), and local breakdown, with patches of relatively rough material, on protruding grains (Fig. 10b). At 300 V, with sparking, craters, in the sub-micron and micron range, typical of dielectric breakdown, were evident generally on all graines. EDX analyses, using an accelerating voltage of 13 kV, revealed oxygen, phosphorus and sodium, from the electrolyte, and titanium, from the substrate (Fig. 11). Carbon and chlorine contaminants were also present. The apparent atomic

percentages of phosphorus were 0.33, 0.84 and 7.92 at% for anodizing at 50, 150 and 300 V respectively.



Fig.10. Scanning electron micrographs of titanium anodized (a) at 50 V, (b) at 150 V, (c) at 300 V in 0.052 M  $Na_3PO_4$  electrolyte at 20°C for 15 min. a, b – secondary electron images; c- backscattered electrons image.

## 3.4.3. X-ray diffraction

XRD of specimens anodized at 20 mA/cm<sup>2</sup> (125 mA/in<sup>2</sup>) (Fig.12a) revealed anatase and rutile, in addition to about 50% of amorphous material as estimated by integral peak areas. About ~98% of the crystalline phase was anatase, as determined by the relative intensities of the characteristic lines referenced to a corundum standard from the International Centre for Diffraction Data. Line broadening indicated crystallite sizes about 9 nm. At 100 mA/cm<sup>2</sup> (625 mA/in<sup>2</sup>), an increased presence of rutile is indicated (Fig.12b), together with relatively low amounts of TiP<sub>2</sub>O<sub>7</sub> and Ti<sub>3</sub>O<sub>5</sub>. The amount of the latter phases have not been quantified, since the previous method is reliable only for a two-phase system.



Fig.11. EDX spectra of titanium anodized at (a) 50 V, (b) 150 V, (c) 300 V in  $0.052 \text{ M Na}_3\text{PO}_4$  electrolyte at  $20^\circ \text{C}$  ( $68^\circ \text{F}$ ) for 15 min.



Fig.12. X-ray diffraction data of titanium anodized in  $0.026 \text{ M Na}_3\text{PO}_4$  electrolyte at  $20^\circ\text{C}$  (68°F) for 20 min. (a) 20 mA/cm<sup>2</sup> (125 mA/in<sup>2</sup>), (b) 100 mA/cm<sup>2</sup> (625 mA/in<sup>2</sup>). Only the peaks additional to those of (a) are indicated in (b).

#### 3.5. Sequential anodizing

EPMA examination of a specimen anodized firstly in 0.026 M Na<sub>3</sub>PO<sub>4</sub> at 100 mA/cm<sup>2</sup> (625 mA/in<sup>2</sup>) for 20 min and then in 0.1 M Na<sub>2</sub>WO<sub>4</sub> at 20 mA/cm<sup>2</sup> (125 mA/in<sup>2</sup>) for 20 min revealed a coating of 11  $\mu$ m (0.44 mil) thickness, comprising contributions of 8 and 3  $\mu$ m from anodizing in the respective electrolytes (Fig.13). The reduced current density in tungstate electrolyte was selected to avoid burning and edge-sparking that can occur when using this solution. Tungsten and titanium species are apparently found in most regions of the film, at the spatial resolution of the technique, about 1  $\mu$ m (40  $\mu$ in.). However, the distribution is non-uniform, with local regions of increased amount of tungsten and associated depletion of titanium. Coatings formed in the individual electrolytes can be distinguished readily by their visual

appearance. The sequentially anodized specimen retained the appearance of a coating formed in the phosphate electrolyte, suggesting comparatively little growth of new film at the coating/electrolyte interface: surface mapping indicated only isolated spots of high concentrations of tungsten.



Fig.13. Electron probe microanalysis of the coating produced by anodizing first at 100 mA/cm<sup>2</sup> (625 mA/in<sup>2</sup>) in 0.026 M Na<sub>3</sub>PO<sub>4</sub>, followed by anodizing at 20 mA/cm<sup>2</sup> (125 mA/in<sup>2</sup>) in 0.1 M Na<sub>2</sub>WO<sub>4</sub>.
(a) backscatterd electron image, (b) titanium distribution map, (c) tungsten distribution map

## 4. Discussion

## 4.1 Coating composition

The present PEO coatings formed in phosphate electrolytes comprise amorphous material, but with significant amounts of anatase and to a lesser extent rutile. The contribution of rutile, and other minor crystalline components, increases with anodizing at increased current density. The amorphous material is presumed to be based on TiO<sub>2</sub>, with incorporated phosphorus species, at least in some regions. Anodic titania is initially amorphous, with crystalline phases, usually anatase, developing at about 20 V, leading to oxygen generation within the film and local

breakdown as oxygen is released. The anatase forms at, or close to, the metal/oxide interface<sup>13</sup>. The present work suggests that the development of the crystalline material may depend upon the orientation of the titanium grains, possibly due to influences of impurities on the morphology and composition of their surfaces during chemical polishing. The growth of amorphous titania results from migration Ti<sup>4+</sup> and O<sup>2-</sup> ions, with a cation transport number of about 0.35<sup>14</sup>. Ionic transport in crystalline anodic oxides is dominated by anion migration, probably involving short-circuit paths. Under PEO conditions, anatase and rutile may also form by transformation of amorphous oxide due to local heating. Rutile is the stable phase at increased temperature, forming in the range 700-1200°C <sup>9</sup>. Ionic migration in crystalline anodic oxides normally requires a relatively high electric field, such that in mixed phase oxides, ionic current possibly flows preferentially through amorphous material<sup>15</sup>.

## 4.2 Coating efficiency

The total charge passed during PEO treatment is consumed in the following reactions at the anode:

$$2Ti + 2H_2O = TiO_2 + 4H^+ + 4e^-;$$
 (1)

$$4OH^{-} \rightarrow O_{2} + 2H_{2}O + 4e^{-}$$
(2)

The growth rates of the PEO coatings evidently diminish with time of treatment at 20 mA/cm<sup>2</sup> in the breakdown region and there is a further reduction in rate for increased current density; Tables 2 and 3 give the efficiency of coating growth expressed as the ratio of the measured coating thickness per unit of charge passed to the calculated value for formation of TiO<sub>2</sub> of density 3.8 g<sup>-</sup>cm<sup>-3</sup>, i.e. that of anatase (see also Figs 14 and 15).

The efficiency values are averaged over the anodizing time, whereas, in practice the efficiency reduces with time. The actual efficiency between 40 min and 60 min at 20 mA/cm<sup>2</sup> is about 1%, compared with the average efficiency of roughly 20%, reflecting the low final rate of thickening of the coating. The tabulated efficiencies are probably upper limits, since the measurement method may overestimate thicknesses due to coating roughness. In addition, coatings contain porosity associated with breakdown events, while amounts of phosphorus species are greater in thicker coatings, thereby lessening contributions of titanium species.

The loss of efficiency with increase of either treatment time or current density is associated with oxygen generation and losses of titanium from the specimens, through physical, chemical or electrochemical processes. The solution concentration of titanium ions, from ICP-OES, corresponds to less than 1% of the weight loss. However, losses to solution probably exceed the levels indicated by the analyses, since colloidal material, undetectable by ICP-OES, settles after leaving the used phosphate electrolytes for 24 h following the PEO treatment.



Fig.14. Dependence of anodizing current efficiency on charge density in  $Na_3PO_4$ , electrolyte at a constant current of 20 mA/cm<sup>2</sup> (125 mA/in<sup>2</sup>).



Fig. 15. Dependence of current efficiency on current density in 0.026M Na<sub>3</sub>PO<sub>4</sub>, anodizing time 20min.

Notably, the solubility product of  $Ti(OH)_4$  is very low 63<sup>-10<sup>-52</sup></sup>. Further, the chemical equilibrium of the electrolyte also involves phosphates and hydrophosphates, with hydrolysis of Ti(IV) species forming colloidal solutions<sup>16</sup>.

The mass balance of coating formation can be expressed as

$$\mathrm{Ti}^{\mathrm{sol}} = (m_1 - m_2) + \mathrm{An}^{-1}$$
(5)

where Ti<sup>sol</sup> is the mass of titanium lost to the electrolyte,  $m_1$  is the initial mass of the specimen,  $m_2$  is mass following PEO; and An<sup>-</sup> is the mass of anion species incorporated into the coating. The initial and final weights are similar for treatments in the 0.026 M electrolyte. Thus, the titanium lost can be estimated from the anion content of the coating, assuming as previously formation of titania. On the basis of Faraday's law, about 9% of the charge is lost through this route for a coating formed at 20 mA cm<sup>-2</sup> in the more dilute electrolyte, with 60% being associated with generation of oxygen. For the more concentrated electrolyte, losses to solution account for the main reduction in efficiency, about 80%, with influence of oxygen generation being relatively minor. Low efficiency in alkaline electrolytes has been reported earlier<sup>27</sup>.

The increased losses of titanium to solution in the 0.052 M electrolyte took place in association with persistent travelling sparks, suggesting that the main losses of titanium occur through breakdown channels. Lower losses of titanium in the 0.026 M electrolyte are presumed to be related to the reduced life-time of individual breakdown sites.

### 4.3 Transport of coating species

Following sequential anodizing, the tungsten tracer was distributed in most regions of the coating at the spatial resolution of EPMA, about 1  $\mu$ m. The tracer originates in the tungstate ions of the electrolyte, which if incorporated into a conventional amorphous anodic oxide would migrate inward through the oxide bulk, with migration not involving short-circuit paths<sup>17</sup>. Hence, the tracer would be normally found in an outer region of the oxide, of thickness related to the migration rate of the anions. In the case of crystalline oxide, migration by short-circuit paths is conceivable, with tungstate ions penetrating close to the region of the metal/oxide interface. However, incorporation of tungsten species into conventional anodic films results in their transformation under the electric field to a cation species that migrates outward. Further, anodic oxidation of Ti-W alloys, with formation of amorphous oxide, discloses that the tungsten species are slower moving than titanium species<sup>18</sup>. Thus, such species derived from the electrolyte are expected to be present in an outer layer of oxide.

Evidently, the distributions of tungsten species in the PEO coating is contrary to expectations from behaviour of tracers in conventional amorphous anodic oxides. Transport by short-circuit paths is important, enabling the tracer to reach the inner regions of the coating. Such paths may be related to the presence of crystalline material, with the associated presence of grain boundaries and amorphous/crystalline interfaces, porosity and cracks, and channels generated by coating breakdown<sup>13</sup>. Regarding porosity, oxygen gas is generated at anatase nanocrystals<sup>19</sup>, with consequent formation of oxygen bubbles within the oxide, the gas being at high pressure. Such gas generation leads to film breakdown below the sparking voltage. Gas generation within the coating may also play a role in initiating breakdown process in the range of sparking voltages. The behaviour of Al-Fe alloys suggests that oxygen generation may also arise due to iron impurity in the substrate, with incorporation of iron species modifying the electron levels in the oxide to facilitate oxidation of O<sup>2-</sup> ions of the oxide<sup>20</sup>. Gas bubbles can also arise due to nitrogen impurity, with evidence of N<sub>2</sub>O forming during anodic oxidation of NbN alloys<sup>21</sup>.

## 4.4 Breakdown voltages

Various definitions of the breakdown voltage quantities are present in the literature. A number of criteria, namely the appearance of visible sparking<sup>23</sup>, a drop of current efficiency<sup>19</sup>, the formation of crystalline phases<sup>12</sup>, the achievement of a maximum stable voltage<sup>24</sup>, the rapid voltage fluctuating<sup>25</sup>, have been variously used to identify onset of breakdowns.

In the present work sparking commenced at 220 and 290 V for 0.052 and 0.026M phosphate electrolytes respectively, marked by the appearance of rapidly moving fine sparks. The sparking voltage did not depend on current density, which is in agreement with reported earlier<sup>23, 26</sup>. A decreased sparking voltage for increased conductivity of electrolyte is well known, with a higher forming voltage promoting a more uniform, dense coating as a result of more numerous, evenly distributed micro-arc discharges<sup>22</sup>.

The form of the dependence of the final forming voltage ( $U_{form}$ ) on current density is still debated. According to the avalanche theory of micro-arc discharge<sup>11</sup>, a stable final voltage is reached when the thickness of undamaged film is sufficient for avalanching to occur across the whole surface. This thickness depends on the field strength, which increase insignificantly with current density<sup>26</sup>. A slight decrease of  $U_{form}$  for a 100 times increase of current density was observed for aluminium<sup>24</sup>. On the other hand, the relationship  $U_{form}=A+B\cdot Ln(j)$  resulting from the present experiments is in agreement with the other works<sup>19, 27</sup> and does not contradict the well-known high field-assisted ionic transport mechanism<sup>28, 29</sup>.

## 5. Conclusions

- 1. The growth of PEO coatings on titanium in alkaline orthophosphate electrolyte at 20°C depends strongly on the process parameters, including current density, electrolyte concentration and charge passed.
- 2. Coatings comprise anatase and rutile, and amorphous TiO<sub>2</sub>, with amounts of rutile increasing with increase of current density. Minor amounts of other crystalline compounds develop at higher currents.
- 3. The efficiency of coating growth decreases with progress of treatment, and is less than 10% for coatings above about 5  $\mu$ m thick.
- 4. The initial breakdown of the coating is dependent upon the orientation of the grains of titanium in the substrate.
- 5. The growth of the coatings involves ready penetration of electrolyte species to most regions of the coating thickness, indicating short-circuit transport paths.

## Acknowledgments

The authors are grateful to the Engineering and Physical Sciences Research Council for support of this work.

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