

## Titanium Dioxide (TiO<sub>2</sub>) Films by Anodic Oxidation in Phosphoric Acid

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**Abstract.** Anodic oxidation is an electrochemical method for the production of an oxide film on a metallic substrate. It involves the application of an electrical bias at relatively low currents while the substrate is immersed in an acid bath. The films can be very dense and stable, with a variety of microstructural characteristics. In the present work, films of the anatase polymorph of TiO<sub>2</sub> were formed on high-purity Ti foil (50 µm thickness) using phosphoric acid (0.3 M H<sub>3</sub>PO<sub>4</sub>). The conditions of oxidation involved the application of potentials (5 to 350 V) and current densities (5 to 60 mA.cm<sup>-2</sup>) for 10 min at room temperature. The films were characterised using a digital photography, laser Raman microspectroscopy, and field emission scanning electron microscopy. The thicknesses of the oxide films on Ti were measured using a thin film analyser based on optical spectroscopy principles. The colours, thicknesses, and microstructures of the films depended strongly on the applied voltage and current density. At bias more than 15 V, single-phase anatase was observed to form on Ti at low (5 mA.cm<sup>-2</sup>) and higher (up to 60 mA.cm<sup>-2</sup>) current density.

### Introduction

Titanium and anodised titanium are used in a range of applications, including aerospace and chemical industries; they are also important in the biological and dental fields [1,2]. It is well known that titanium invariably has a nanoscale (1.5-10 nm thickness) passivating layer on the surface, which forms spontaneously upon exposure to air [3]. This layer typically consists of oxides and hydroxides that form from reactions between the metal substrate and humid air [4].

A comparable protective layer can be formed under controlled conditions using anodic oxidation, which is a well established method of modifying the surface microstructure and the properties of titanium. This electrochemical approach for protective layer formation can be used to produce much thicker layers on titanium (up to several hundred microns thick) and these layers may be amorphous or crystalline, dense or porous, depending on the electrolyte, its concentration, and applied potential [5]. The electrolytes most commonly used to anodise titanium are sulphuric and phosphoric acids [6].

### Experimental Procedures

**Sample Preparation.** High-purity Ti foils of dimensions 25 mm x 10 mm x 0.5 mm were wet hand-polished using 1200 grit (~1 µm) abrasive paper, followed by immersion in an ultrasonic bath with acetone, rinsing with distilled water, and drying with compressed air.

**Anodisation.** Anodic oxidation was done in an electrochemical cell containing ~0.4 L aqueous solutions of H<sub>3</sub>PO<sub>4</sub> (Univar, 85 wt%) at ~25°C [7]. These solutions and the associated experimental parameters are shown in Table 1. The anode and cathode were Ti foil and the anodising was done with a programmable power supply (EC2000P, E-C Apparatus Corp., USA). The anodised foils were cleaned by dipping in distilled water and then dried in still air.

Table 1 Parameters used for anodic oxidation in  $\text{H}_3\text{PO}_4$ .

Parameter	Value(s)
$\text{H}_3\text{PO}_4$ Electrolyte (Molar)	0.3
Temperature ( $^{\circ}\text{C}$ )	$\sim 25$
d.c. Voltage (V)	5, 10, 20, 30, 40, 50, 70, 100, 150, 200, 250, 300, 350
Current Density ( $\text{mA cm}^{-2}$ )	5, 10, 20, 40, 60
Duration (min)	10
Conductivity ( $\text{S cm}^{-1}$ )	18.92

**Characterisation.** The colours were recorded using a digital camera (Olympus  $\mu 725\text{SW}$ ). The mineralogical compositions of the films were determined using Raman microspectroscopy (Renishaw MK1 Raman Microscope) with red laser wavelength of 632.8 nm. The thicknesses were measured using a thin film analyser (Mikropack NanoCalc-2000). The microstructures were examined using a field emission scanning electron microscope (FESEM, Hitachi, Model S4500 II) at an accelerating voltage of 20 kV.

## Results and Discussion

### Colour of Anodic Films

The visual appearance of films as a function of applied voltage and current density is shown in Figure 1. According to multiple-beam interference theory [8], the colouring results from the interference between the light beams that are reflected from (a) the film surface and (b) the film-substrate interface. Delplancke *et al.* [8] showed that the colour of titanium oxide was principally dependent on the anodic oxide thickness. Sul *et al.* [5] suggested that other factors could influence the colours, even when the oxide film thickness is almost same. These factors are: type of electrolyte, electrolyte concentration, crystal structure, oxide density, and defect density [9]. The data allow the following conclusions to be made:

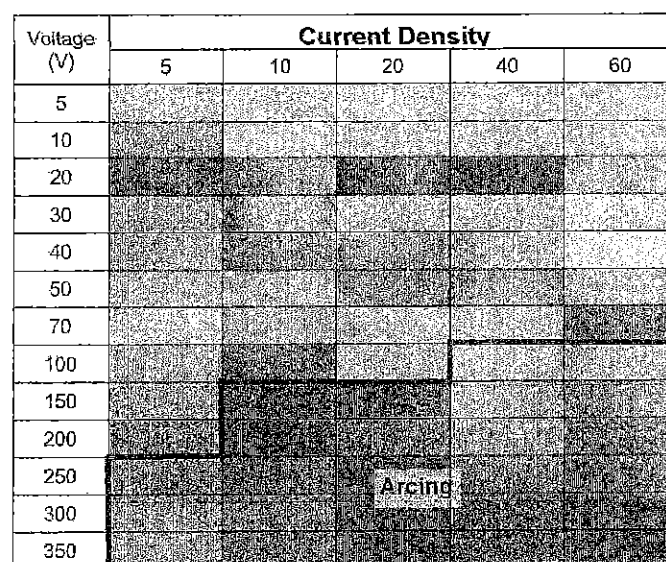


Fig. 1 Colours of film surfaces (0.3 M  $\text{H}_3\text{PO}_4$  electrolyte) as a function of applied voltages and current densities.

- At  $< 30$  V, the colour and brightness are constant for each voltage but there is effect as a function of the current density.
- The colour and brightness effects for voltages  $\geq 30$  V are variable.
- Arcing occurred and contributed to the grey colour as indicated by the blue border.

- There is no clear colour effect as a function of the voltage up to 200 V
- Arcing was observed consistently at voltages  $\geq 250$  V, resulting in constant colour and brightness.

### Microstructure (FESEM)

Figure 2 shows FESEM images of the films as a function of the applied voltage, while Table 2 summarises the data in the figure. The table indicates that there are five stages of microstructural development.

Table 2 Effect of voltage on microstructure

Voltage Range		Type of Microstructure	Relevant Phenomenon
Type	Volts		
Very low	5	Incomplete	Onset of film growth
Low	10	Dense and smooth	Monolayer formation
Intermediate	20-70	Dense and uneven	Increasing film growth
High	100	Pore formation	Onset of arcing
Very High	150-350	Variable porosity	Subsurface arcing

More specifically, the five stages of film growth can be described as follows:

- *Very Low Voltages:* Commencement of oxidation, resulting in an incoherent surface film.
- *Low Voltages:* Formation of a monolayer-scale film of anatase of  $\sim 3$  nm thickness.
- *Intermediate Voltages:* Increasing but uneven film growth probably resulting from enhanced growth along the scratches and other defects formed by polishing.
- *High Voltages:* Pore formation occurs due to dielectric breakdown [10] as shown subsequently in Figure 2.
- *Very High Voltages:* Consistently increasing pore size owing to regular dielectric breakdown and accompanying porosity increase (size and amount), as discussed subsequently.

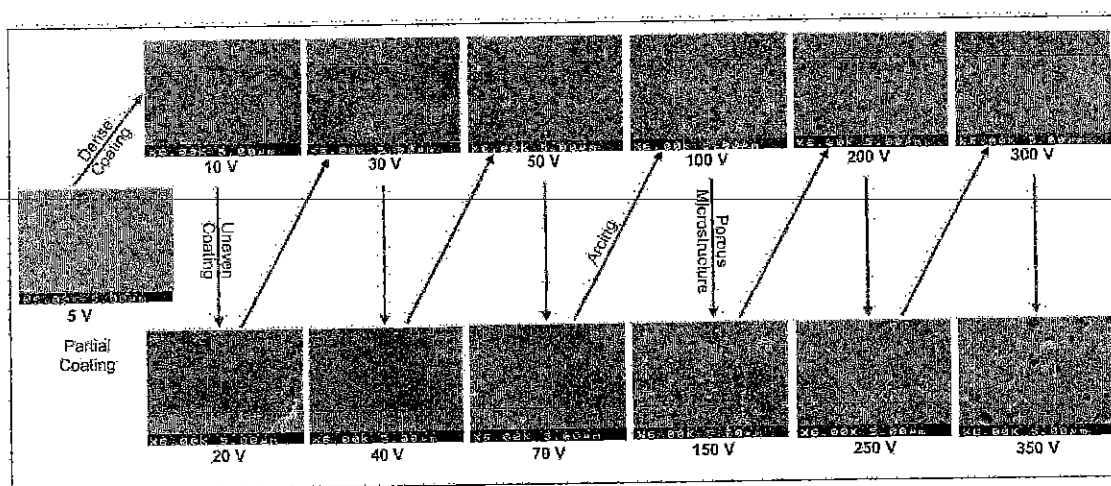


Fig. 2 FESEM images of the film surfaces (0.3 M  $\text{H}_3\text{PO}_4$  electrolyte) as a function of the applied voltage at  $40 \text{ mA}\cdot\text{cm}^{-2}$ .

Figure 2 shows that, upon the onset of arcing and porosity formation, the appearance of the anodic film surface changes gradually with increasing applied voltage. The pore size and amount clearly increased with applied voltage. A similar result was obtained by Kuromoto *et al.* [11] for titanium anodically oxidised in 1.4 M  $\text{H}_3\text{PO}_4$  electrolyte. A solution of low concentration of  $\text{H}_3\text{PO}_4$

resulted in smaller pores relative to a high acid concentration. Frauchinger *et al.* [11], reported that low-concentration  $\text{H}_3\text{PO}_4$  solution (0.01 M) produced a very fine surface structure with small pores on titanium. This was attributed to the use of a low concentration and the associated low electrical conductivity of the electrolyte.

### Mineralogy (Laser Raman Microspectroscopy) and Thickness

Figures 1 and 3 show the following colours and mineralogical results:

- Laser Raman microspectroscopy indicated that anatase was observed at  $\geq 20$  V.
- The relative amount of anatase formed is a function of both or either the thickness and/or the crystallinity of the films [12].
- With increasing voltage, the peak intensities increased, indicating increasing levels of anatase (thickness) and/or increasing crystallinity. Sul *et al.* [13] have observed amorphous titania on the surface of anodised titania, so it is possible that the latter contributes to the intensity increase.
- The films were similar to those produced with  $\text{H}_2\text{SO}_4$  [7]. This was a function of the oxidising power of the electrolyte.
- Alternatively, the explanation may lie in the observation that anodic oxide growth behaviour is determined by the electrochemical dynamics between the ability of an oxide film to form and its tendency to dissolve in the electrolyte [13]. Since  $\text{H}_3\text{PO}_4$  is the strongest oxidising agent, it also can be considered the strongest solvent. These competing mechanisms may be responsible for the apparent non-linearity of the data in the region 30-70 V.

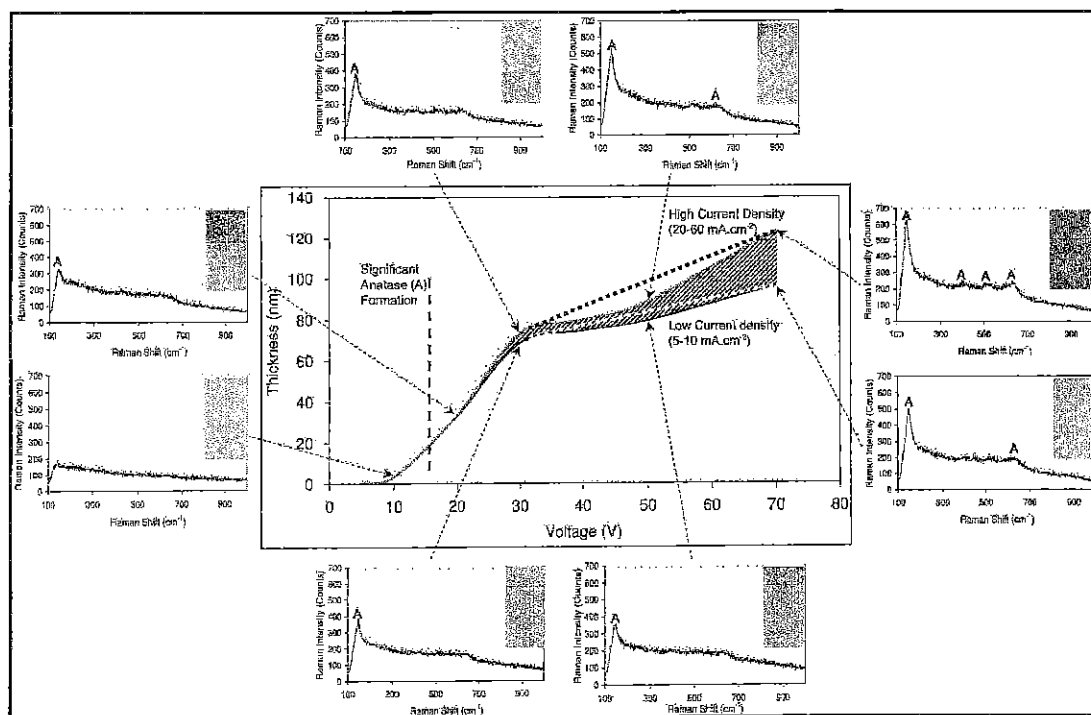


Fig. 3 Film thickness as a function of applied voltage, shown through laser Raman microspectroscopy patterns (A=anatase, main peak at  $144\text{ cm}^{-1}$ ), interference colours, onset of detectable anatase formation, and effect of current density.

Figures 4 and 5 show that anatase is the only phase formed at voltages of 100-350 V for current densities  $5\text{ mA.cm}^{-2}$  and  $60\text{ mA.cm}^{-2}$ . The intensities of the peaks increased with increasing applied voltage. Examination of the appearance of the peaks does not support the conclusion of increasing crystallinity since the peak widths remain approximately constant with increasing voltage.

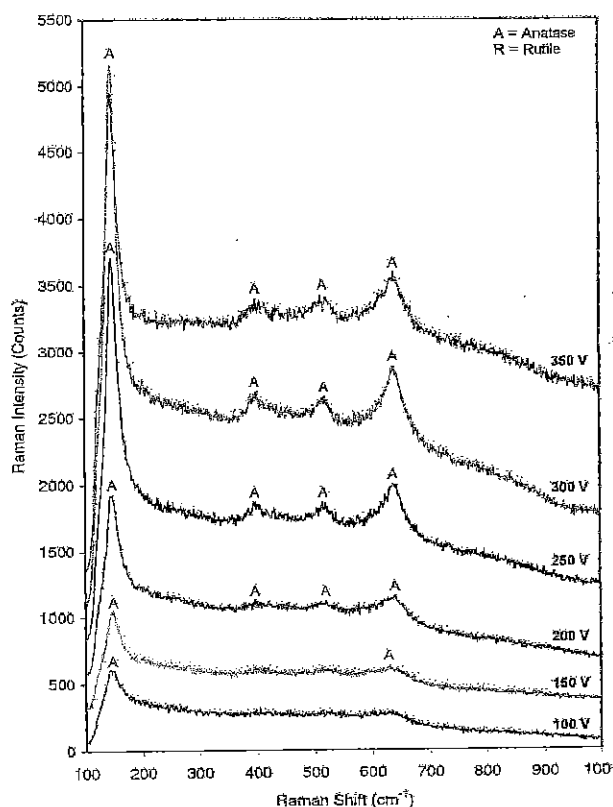


Fig. 4 Raman spectra of anodic films at 5  $\text{mA.cm}^{-2}$  in solution of 0.3 M  $\text{H}_3\text{PO}_4$  for 100, 150, 200, 250, 300, and 350 V.

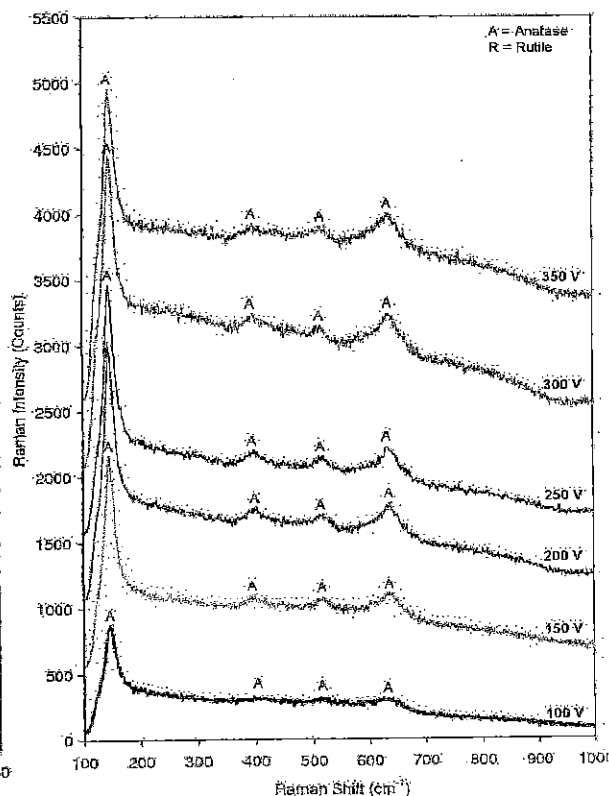


Fig. 5 Raman spectra of anodic films at 60  $\text{mA.cm}^{-2}$  in solution of 0.3 M  $\text{H}_3\text{PO}_4$  for 100, 150, 200, 250, 300, and 350 V.

The current density data are not consistent in that the amount of anatase would be expected to be greater for the higher current density. However, this is the case only for the range 100-200 V (and for 30-70 V, as shown in Figure 3; the converse is the case for 250-350 V. The reason for this probably resulted from the fact that the laser beam was of diameter  $\sim 1 \mu\text{m}$  and this was in the size range of the porosity. With higher current densities, more arcing and large pore generation occurred. Thus, it is likely that the apparent intensity decrease resulted from the scanning of more pores than the case for the less porous microstructures produced at the lower current densities.

## Conclusions

The colours of the films result from (a) interference effects associated with the thicknesses at low voltages and (b) partial reduction of titania at high voltages. Interference colours include yellow, blue, purple and green; reduced titania is grey. All of the films consist of anatase, with the rate of formation becoming significant at  $\geq 20$  V. The thicknesses of the films reach 120 nm at 70 V, increasing sigmoidally as a function of increasing voltage. Titanium can be anodised using a basic power supply and acid solutions. The resultant thin films show five stages of growth as a function of voltage and they can be described by specific microstructural characteristics. The dominant features of these stages are the production of (a) dense and uneven films at low voltages and (b) porous films that result from arcing at high voltages.

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