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Preparation and Characterisation of TiO_2 Thick Films Fabricated by Anodic Oxidation in Sulphuric Acid

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Abstract **-** Anodic oxidation is an electrochemical method for the production of oxide films on metallic substrates. It involves the application of an electrical bias at relatively low currents while the substrate is immersed in an acid bath. The resultant oxide films can be very dense and stable, showing a variety of colours and microstructural characteristics. In the present work, thick films of the anatase and rutile polymorphs of TiO_2 were formed on high-purity Ti foil (50 μm thickness) using sulphuric acid solutions (1.5 M H_2SO_4). The conditions of oxidation involved the application of potentials (5 to 350 V) and current densities (5 to 60 $mA.cm^{-2}$) for 10 min at room temperature. The films were characterised using a digital photography, laser Raman microspectroscopy, and field emission scanning electron microscopy (FESEM). The thicknesses of the oxide films on Ti were measured using a thin film analyser based on optical spectroscopy principles. The phase formation, colours, thicknesses, and microstructures of the films depended strongly on the applied voltage and current density. At a standard bias of 150 V, single-phase anatase was observed to form on Ti at low current density (5 $mA.cm^{-2}$) but, at higher current densities (up to 60 $mA.cm^{-2}$), increasing rutile formation was observed.

Keywords**:**

I. 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 most commonly used electrolytes are dilute solutions of sulphuric acids at low (>100 V) or high (~100-250 V) potentials.

II. METHODS AND PROCEDURES

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. Anodic oxidation was done in an electrochemical cell containing ~0.4 L aqueous solutions of H_2SO_4 (Merck, 98 wt%) at ~25°C [6]. 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.

The colours were recorded using a digital camera (Olympus μ725SW). 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.

Table 1:Parameters used for anodic oxidation in H_2SO_4.

Parameter	Value(s)
H_2SO_4 Electrolyte (Molar)	1.5
Temperature (°C)	~25
d.c. Voltage (V)	5, 10, 20, 30, 40, 50, 70, 100,150, 200, 250, 300, 350
Current Density ($mA.cm^{-2}$)	5, 10, 20, 40, 60
Duration (min)	10
Conductivity ($S.cm^{-1}$)	>0.20 (for 1.5 M; off-scale of pH meter)

II. RESULTS AND DISCUSSION

Colour of Anodic Films

The visual appearance of the films as a function of applied voltage and current density is shown in Figure 4.1. According to multiple-beam interference theory [7], 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*. [7] 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
- Defect density [8].

The present data allow the following conclusions to be made:

- Although interference colours are inevitably influenced by the nonuniformity of the films [3], the uneven surfaces are of insufficient thickness variation to allow for the detection of colour variation by visual assessments; *i.e.*, the smoothness of each sample surface appears to be relatively consistent.
- There is no gradual colour variation as a function of the applied voltage, associated film thickness (see following), or interference effects.
- There is no colour effect as a function of the current density for applied voltages <40 V.
- At applied voltages ≥40 V, the colour varies as a function of current density.
- Arcing and the consequent localised melting are associated with the generation of grey colour, which probably results from partial reduction [9] associated with the localised melting. Reduction occurs since O_2 is lost during arcing (spark production and associated oxidation).
- Anatase converts to rutile at voltages ≥150 V and at 60 $mA.cm^{-2}$, suggesting that the temperatures associated with arcing exceed ~400°-1100°C, which is the range reported for the anatase - rutile transformation [10].

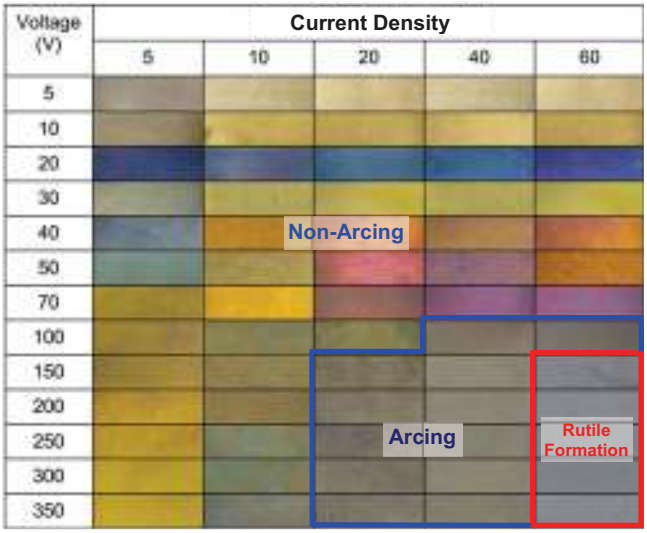

Figure 4.1: Colours of film surfaces (1.5 M H_2SO_4 electrolyte) as a function of the applied voltage and the current density.

- The arcing commences at 100 V; Figure 4.1 indicates that arcing also occurs only at a current density ≥20 $mA.cm^{-2}$. This arcing occurs due to dielectric breakdown (rapid reduction in the resistance of an electrical insulator) [11]. According to these authors, [11] dielectric breakdown occurs in the range of 80-240 V in H_2SO_4.
- The sample as the lowest voltage and current density is grey because the anodised layer was so thin that the metallic titanium colour dominates.

Based on Figure 4.1, these results can be summarised as follows.

- 5 V All grey owing to titanium visible through very thin layer of homogeneous thickness.

- 10 V All yellow owing to onset of visible film formation. The same results have been obtained by others [12]. Again, the layer remains relatively thin and of homogeneous thickness.
- 20 V All blue owing to consistent growth in thickness of still relatively thin layers of homogeneous thickness.
- 30-70 V Variable colours owing to variable thicknesses resulting from differential growth rates and resultant greater thicknesses that interact more readily with visible light wavelengths.
- ≥100 V (i) 5 mA.cm^{-2}: All yellow owing to thin layers associated with low current densities. (ii) ≥10 mA.cm^{-2}: Essentially all grey owing to onset of arcing and consequent partial reduction.

Some of the results of the present work are similar to those reported by Diamanti *et al*., [12], who found that the maximal brightness was at ~60-70 V and minimal brightness at 20 V and 100V. When a particular thickness is reached, the same interference conditions are achieved, resulting in a repetition of colours.

Mineralogy (Laser Raman Microspectroscopy)

Laser Raman microspectroscopy was used as the assessment tool for the mineralogy because the early-stage formation of anatase can be detected more readily since this method is more sensitive than XRD. Figures 4.1 and 4.4 show the following colour and mineralogical results:

- Laser Raman microspectroscopy data indicated that anatase levels (of sufficient concentration to be detected by this method) were observed at ≥30 V.
- The relative amount of anatase formed is related to the thickness of the films, which is expected for this confocal beam method of analysis [6].
- However, the increase in peak height as a function of applied voltage and thickness also may be due in part (or wholly) to the increasing crystallinities of the films, which are assessed by this method of analysis [6].

Figure 4.2 shows that anatase is the only phase formed at applied voltages of 100-350 V and 5 mA.cm^{-2}. The intensity of the major peak increased with increasing applied voltage. This means that the amount and/or crystallinity of anatase are/is influenced by the applied voltage. The formation of an anatase film was observed even at low current density (5 mA.cm^{-2}) and applied voltage (30 V). Figure 4.9 shows equivalent data for the same voltage range but at the high current density of 60 mA.cm^{-2}. These data show increased levels of anatase and the presence of rutile at all voltages.

Further, Figure 4.3 shows that the size of the rutile peaks increases initially (100 V and 150 V) but becomes more or less constant at higher voltages (200-350 V). This observation provides a useful indication of the penetration (and sensing) depth of the laser beam since increasing film thicknesses with increasing voltage would be expected to result in increasing peak intensities. Since this is not the case, the higher voltages produced films of thickness greater than the penetration depth of the laser.

Examination of Figure 4.2 shows that the intensity of the major anatase peak does not change significantly, indicating that voltage is not critical at low current density. However, examination of Figure 4.3 shows that there is a significant effect of voltage as high current density. Therefore, the primacy of the effect of current density, assessed previously, is confirmed.

Thicknesses

The thickness of the films as a function of the applied voltage (limited to ≤70 V due to equipment limitation) is represented in Figure 4.4. These data reveal the following characteristics:

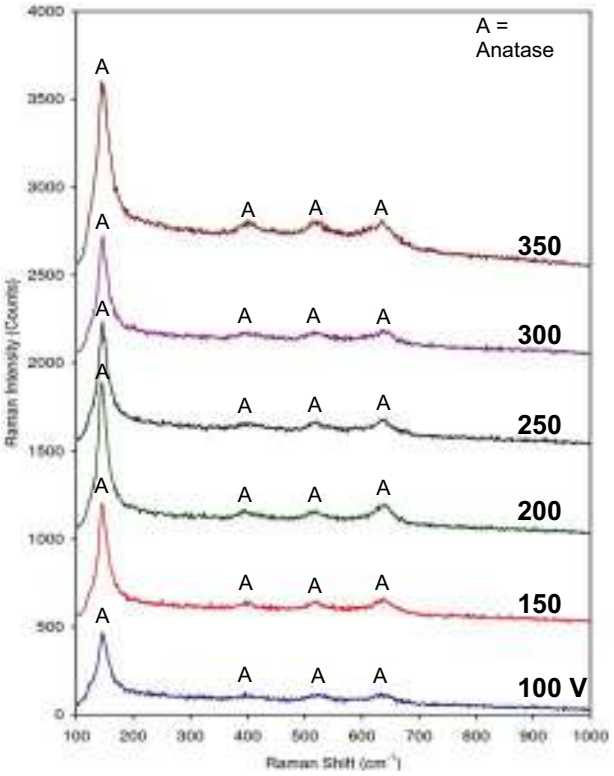

Figure 4.2: Raman spectra of anodic films at 5 mA.cm^{-2} in solution of 1.5 M H_2SO_4 for 100, 150, 200, 250, 300, and 350 V.

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	Variable porosity	Onset of arcing
Very High	150-350	Consistent porosity	Subsurface arcing

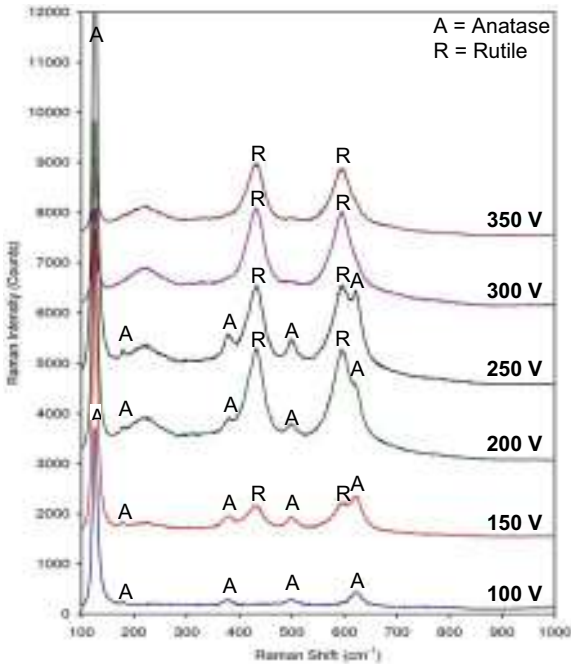

Figure 4.3: Raman spectra of anodic films at 60 mA.cm^{-2} in solution of 1.5 M H_2SO_4 for 100, 150, 200, 250, 300, and 350 V.

- The film thickness increases sigmoidally with applied voltage, yielding thicknesses up to ~130 nm. Such sigmoidal behaviour is observed commonly in many processes, such as gaseous oxidation [13]. However, no other researchers have reported complete kinetics data for anodisation.
- The film thicknesses at current densities of 5 and 10 mA.cm^{-2} are lower than those at the higher current densities (20, 40, and 60 mA.cm^{-2}), the latter of which were fairly consistent in thicknesses. This is because the higher power (voltage and current [density]) assists in the anodisation process.

Microstructure (FESEM)

Figure 4.5 shows FESEM images of the films as a function of applied voltage, while Table 4.2 summarises the data. The table indicates that there are five stages of microstructural development.

Table 4.2: Effect of voltage on the microstructure.

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

- *Very Low Voltages*: Commencement of oxidation, resulting in incoherent surface film.
- *Low Voltages*: Formation of monolayer-scale film of anatase of ~3 nm thickness.
- *Intermediate Voltages*: (a) Increasing but uneven film growth probably resulting from enhanced growth along the scratches formed by polishing (defects). (b) Formation of cracks at 70 V probably resulting from stresses associated with exaggerated growth at pits formed during polishing, followed by chemical attack of the substrate by the electrolyte and potential weakening of the film-substrate bond by undercutting.
- *High Voltages*: (a) Onset of formation of pores probably due to the dielectric breakdown [14] and consequent imposition of temperatures sufficient to melt the film [15]. (b) Presence of pores allowing access to substrate by the electrolyte, consequent chemical attack, and potential lowering of the adhesive strength of the film by undercutting.
- *Very High Voltages*: Establishment of a consistent porous microstructure of thickness >9.2 μm, determined by the current density (current set on the controller divided by the total surface area of the anode).

COCLUSIONS

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 ≥30 V. However, at 150 V, rutile formation also occurs owing to the heat associated with the arcing. The thicknesses of the films reach 130 nm at 70 V, increasing sigmoidally as a function of increasing voltage. While the higher cut-off amperages yield greater thicknesses than do the lowest cut-off amperage, the effect of acid concentration is not consistent. 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 smooth films at low voltages and (b) porous films that result from arcing at high voltages.

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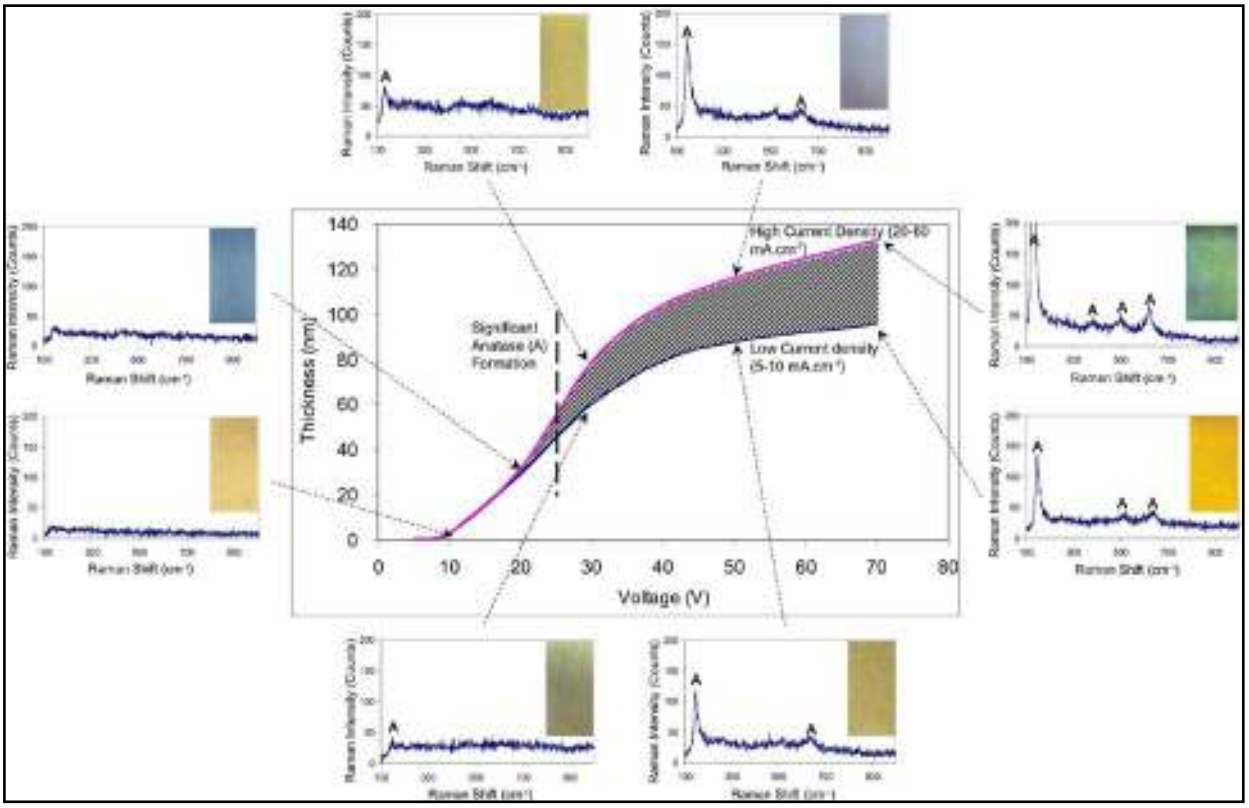

Figure 4.4: Film thickness as a function of applied voltage, shown through laser Raman microspectroscopy patterns (A=anatase, main peak at 144 cm^{-1}), interference colours, onset of detectable anatase formation, and

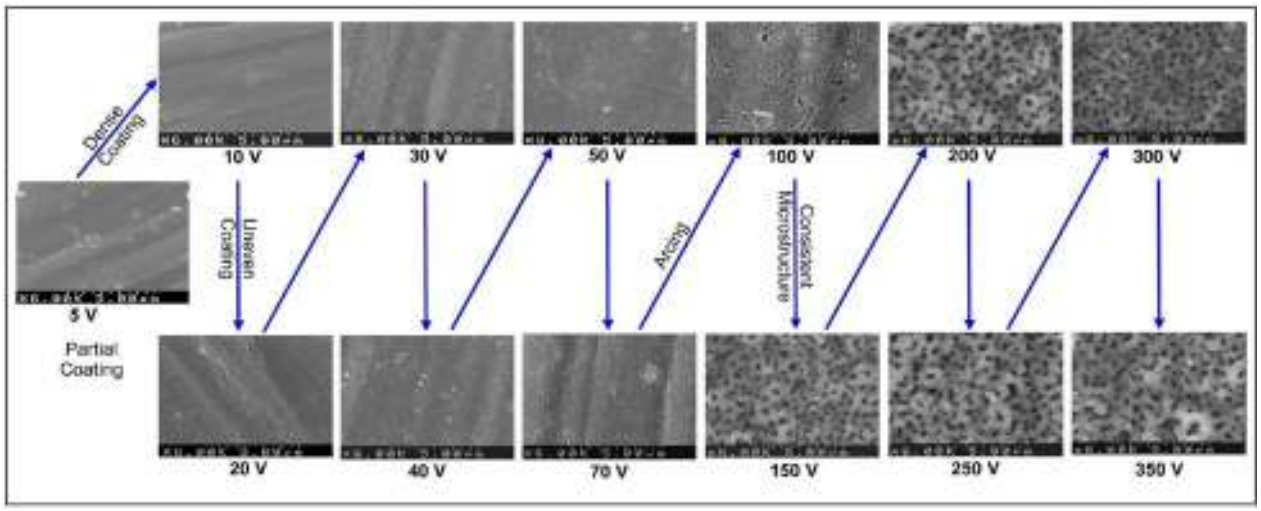

Figure 4.5: FESEM images of film surfaces (1.5 M H_2SO_4 electrolyte) as a function of applied voltage at 40 $mA.cm^{-2}$