

The Anatase Formation on Anodised Titanium in Sulphuric Acid

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Abstract

Anodic oxidation is used to evaluate the effects of pure titanium in a sulphuric acid electrolyte in order to evaluate the relationship between the TiO₂ anatase crystalline phase formation and anodization parameters. Multiple characterisation techniques were used and found that the thickness showed significant increase in TiO₂ at 70V, FESEM observed significant porosity at the arcing voltage commencement (100V). XRD analysis observed anatase peak threshold at 70V, However Raman Microscopy showed anatase significance formation between 20V-30V. We conclude that anatase presents at low voltage 20-30V while rutile peaks increase initially (100V and 150V) and the amount and /or crystallinity of anatase are/is influenced by the applied voltage.

Introduction

Anodic oxidation is used to modify the surfaces and properties of titanium (Ti) and aluminium owing to the resultant mechanical properties, corrosion resistance, non-biotoxicity, and biocompatibility [1].

Ti always is coated by an oxide surface layer of 1.5-10 nm thickness, which forms spontaneously upon exposure to air and atmospheric water vapour [2]. Anodic oxidation of Ti allows the controlled production of a protective oxide surface layer much thicker than that formed naturally. These coatings may be dense or porous, amorphous or crystalline, depending on the conditions, such as electrolyte type, solution concentration, and applied potential [3].

Crystalline oxides, that is, anatase and

rutile, present several peculiar features, such as photocatalytic behaviour, super-hydrophilicity and biocompatible properties [4]. The electrolytes most commonly used to anodise Ti are sulphuric and phosphoric acids [5].

This work focuses on the evaluation of the effects of titanium anodic oxidation in a sulphuric acid electrolyte on the formation of TiO₂ crystal phases in the oxide layer; the impact of process parameters modification will be studied, in order to maximize the achievement of these structures, especially for what concerns the anatase form. In particular, the relationship between anatase formation and process parameters will be evidenced [4].

Experimental method

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. Anodic oxidation was done in an electrochemical cell containing ~0.4 L aqueous solutions of H₂SO₄ (%) [1]. The anode and cathode were Ti foil and the anodising was done with a programmable power supply. The associated experimental parameters are shown in Table 1.

Table 1: Parameters Used for Anodic Oxidation of

Parameters	Values
Temperature (C ^o)	25
Electrolyte concentration (Molar)	0.5, 1, 2

DC Voltage	30-120
Current density (mA/cm ²)	5, 10, 20, 40, 60
Duration (min)	1, 3, 5, 10

The microstructures and thicknesses of the films were characterised using (1) Thickness measurement; (2) The microstructures were examined using a field emission scanning microscope (FESEM). (3) Glancing angle x-ray diffraction (XRD) and (4) Raman microscopy.

Results and discussion

The thickness at 1.5M H₂SO₄ shows that at all current densities the thickness starts to increase suddenly from 100 nm at 70 V to about 9 μm at 100 V, from 100V-120 V the thickness varied from 9.2 μm at 10 mA/cm² to about 11.0 μm at 60 mA/cm².

According to FESEM images the microstructure show variable porosity at the onset of arcing voltage 100 V and more while the microstructure shows dense and uneven at voltage between 30-70 V with increase film growth.

XRD show anatase threshold at 70 V at all current densities, up to 100 V and 150 V the rutile start to form.

Laser Raman Microscopy showed significant anatase formation between 20-30V when the thickness is around 50nm, the anatase main peak (144 cm⁻¹) show higher intensity as higher current density (20-60 mA/cm²) as the voltage increases up to 70 V.

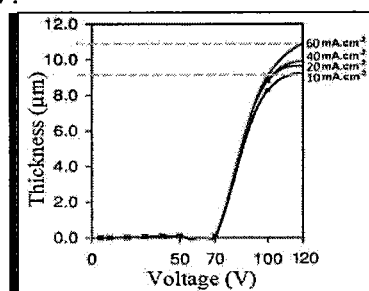


Fig. 1: Thickness of samples oxidised in 1.5 M H₂SO₄ at various voltage for different current density (10, 20, 40, and 60 mA.cm⁻²).

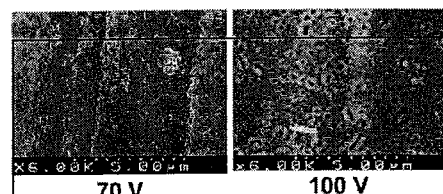


Fig. 2: FESEM images of film surfaces (1.5M H₂SO₄ electrolyte) as a function of applied voltage at 40 mA.cm⁻².

Conclusion

Anatase presents at low voltage 20-30V while rutile peaks increase initially (100V and 150V). The intensity of the major peak increases with higher current densities as the voltage goes higher. That means that the amount and /or crystallinity of anatase are/is influenced by the applied voltage.

References

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