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Tailoring oxide-layer formation on titanium substrates using microwave plasma treatments

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ABSTRACT

Oxides of titanium have found applications in areas such as energy capture, cell attachment to biomedical devices and as catalytic surfaces. This study demonstrates that the use of a microwave plasma can significantly enhance both titanium oxide formation and growth rate, compared with those obtained using conventional furnace treatments. The ability of microwave plasma treatments to control the thickness and morphology of oxides grown on titanium substrates is demonstrated. For a fixed plasma treatment time of 10 min, depending on the input power and treatment pressure, the oxide-layer thickness of between 0.69 and 10.45 μm were obtained. The associated roughness (R_a) values were in the range of 0.11–0.67 μm. This study demonstrated that the morphology of the oxide-layer was particularly influenced by the input power to the plasma, while oxide thickness was depended on the treatment pressure and time. The mechanism of titanium oxidation was also investigated and based on the homogeneous oxidation observed across the titanium metal surface (under the oxide layer), it is also concluded that the mechanism of oxidation is 'general corrosion'.

1. Introduction

Titanium has found application in areas such as aeronautical and medical devices, particularly due to its strength to weight ratio. Like other transition metals titanium is usually covered with a thin layer of native oxide, which forms on exposing the metal to air [1]. This oxide is usually the Anatase phase of Titanium dioxide (TiO_2), which has a tetragonal crystal structure and usually forms with a thickness in the range of 4–10 nm [2,3]. The two other polymorphs of TiO_2 are Brookite and Rutile. The latter exhibits a tetragonal crystal structure, while Brookite has an orthorhombic structure [4–6]. Oxides of titanium either on the metal surface or alternatively as TiO_2 coatings and powders have found applications in areas ranging from medical devices (cell attachment), solar cells (light capture), air and water purification, gas sensing, wear protective coatings, etc. [7–12]. This is due to the oxide's photocatalytic, biocompatibility properties, as well as its physical and chemical stability.

For applications, such as for cell attachment (osteointegration) onto medical devices, thicker titanium oxide layers are desirable, than that which is obtained for the native oxide [13]. The use of chemical and physical treatments has previously been investigated in order to enhance the thickness of this oxide layer on titanium [14–20]. The chemical oxidation methods include the use of electrochemical treatments (anodic oxidation), sol–gel treatment and chemical vapour deposition (CVD) [7]. Using electrochemical treatments, Zwilling et al. [21,22] obtained oxide-layers with structure and morphology either compact and thin (less than 20 nm), or porous and thick (more than 50 nm), depending on the electrolyte used. The importance of electrolyte, current density and applied potential on oxide thickness, structure and morphology obtained using this technique was demonstrated by Diamanti et al. [1].

Non-directly chemical oxidation treatments include the use of furnace treatments, thermal spraying, physical vapour deposition and ion implantation, for which the formation of surface modified layer on titanium and its alloys are mainly attributed to thermal, kinetic and electrical energy [7]. Thermal treatment of titanium has the effect of increasing the oxide layer thickness or/and the transformation of crystalline phases of TiO_2 [23–25]. The Anatase phase is generally formed at temperatures below 600 °C; above this temperature, the Rutile phase is obtained. An early investigation of oxide formation using thermal treatments carried out by Kofstad et al. observed that larger oxide crystals are formed after thermally treating the metal at 1000 °C, compared to those obtained at 900 °C [19]. It also demonstrated that based on cross-sectional studies of oxidised titanium that the first oxide layer formed is dense and homogeneous, however, with increasing thickness the level of porosity in the oxide increases. The growth of the oxide layer using furnace treatments is reported to be relatively slow, for example, Dearnley et al. found that titanium oxide layer thicknesses of 0.8 μm were achieved after treatment in an air furnace at 625 °C, for 36 h [25].

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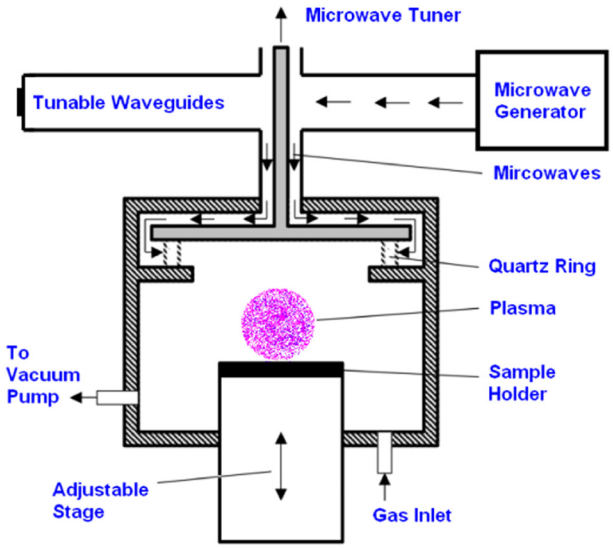

Fig. 1. Schematic representation of the CAP microwave reactor.

There have been a number of reports on the use of plasma treatments to shorten oxidation time to seconds/minutes rather than hours. For example, DC plasma exposure was found to yield titanium oxide layer thicknesses of 30 nm, after 5 min treatment [26]. These authors, however, reported an "oxide thickness saturation" after this treatment time, with a much slower subsequent growth of the oxide.

The use of microwave plasma sources for the oxidation treatment of the surface of titanium and its alloys has potential to be more effective than a DC plasma, because of the higher density of atomic oxygen that can be generated using this type of discharge [27]. Microwave discharges generally have higher electron kinetic temperature and number density because the power is usually coupled through radiation and thus, bypasses sheath losses [28,29]. A further advantage of these plasmas is that they can be operated in a wide gas pressure range [30,31], which combine with the higher electron temperature generally obtained, makes them capable of providing a higher fraction of ionization and dissociation [30]. The use of an electron cyclotron resonance (ECR) microwave plasma operating at 0.11 Pa has previously been reported to lead to an oxide thickness of approximately 3 μm, after a 60-minute treatment time [20]. A further study using a non-ECR microwave discharge operating at 2.4 kW, a substrate temperature of 600 °C and treatment time of 45 min, resulted in an oxide consisting of a mixture of Anatase and Rutile phases, with thickness of 3.5 μm [32].

This study is focused on evaluating how microwave plasma treatment parameters influence the growth, morphology and structure of the TiO_2 layer. Specifically, the effect on oxide growth and morphology are evaluated, with systematically changing the input power and pressure used to generate the plasma as well as the treatment time used. Of particular interest is the investigation how oxide growth and layer thickness, influences the roughness and morphology of the interface between the titanium metal substrate and oxide layer.

2. Materials and methods

A microwave Circumferential Antenna Plasma (CAP) reactor operating at 2.45 GHz was used for the plasma oxidation treatment of titanium discs (Fig. 1). This system is described in detail elsewhere [33]. Commercially pure (CP) titanium blocks (250 mm × 150 mm × 8 mm) were faced and cut into discs (diameter 25 mm and thickness 5 mm), using a Hurco VM3 CNC mill system. These discs were ground and polished to a mirror finish using silicon carbide abrasive paper (240, 320, 600 and 800), diamond suspension (6 and 3 μm) and colloidal silica. They were subsequently cleaned in an ultrasonic bath using methanol and deionised water; blow-dried with air prior to plasma treatment. The resulting test substrates exhibited a roughness of 0.01 μm. The microwave plasma process involved a five-minute pump down to a base pressure of 8 Pa, before the introduction of oxygen into the chamber. The pressure was allowed to rise to 0.6 kPa, before igniting the microwave discharge. The titanium disc was mounted in the plasma using a molybdenum metal holder, which in-turn was supported on a quartz rod. The processing conditions were systematically altered with input powers in the range 0.9 to 2.1 kW, operating pressures between 1.0 and 5.0 kPa and treatment time between 5 and 25 min. Single test coupons were evaluated under each processing condition. The oxygen gas (99.9%) flow rate was maintained at 100 sccm for all treatments.

Temperature measurements were carried out using a LASCON QP003 and LPC03 ratio pyrometers from Dr. Mergenthaler GmbH & Co. KG. The temperature generated on the titanium substrate by the discharge was found to be in the range 716 to 910 °C, depending on the plasma processing conditions used. Oxide-layers were also grown in a 2 kW Carbolite Elf 11/6B furnace for comparison. For this treatment, the titanium disc was heated at a rate of 20 °C/min in air to 790 °C and was then maintained at this temperature for 300 min. The power was then shut off and the part was allowed to cool to room temperature (22 °C) in the furnace.

The morphology of the resulting titanium oxide-layer samples was characterised using an FEI Quanta 3D FEG DualBeam scanning electron microscope (SEM). Cross-section analysis of the oxide layer thickness was obtained using a focused ion beam (FIB) and metallographic technique for comparison (Fig. 2).

To facilitate obtaining the FIB cross-sections, a 2 × 30 μm, 1 μm thick Platinum (Pt) layer was deposited on the surface. A 30 kV Ion beam at a current of 15 nA was used to cut the initial cross-section

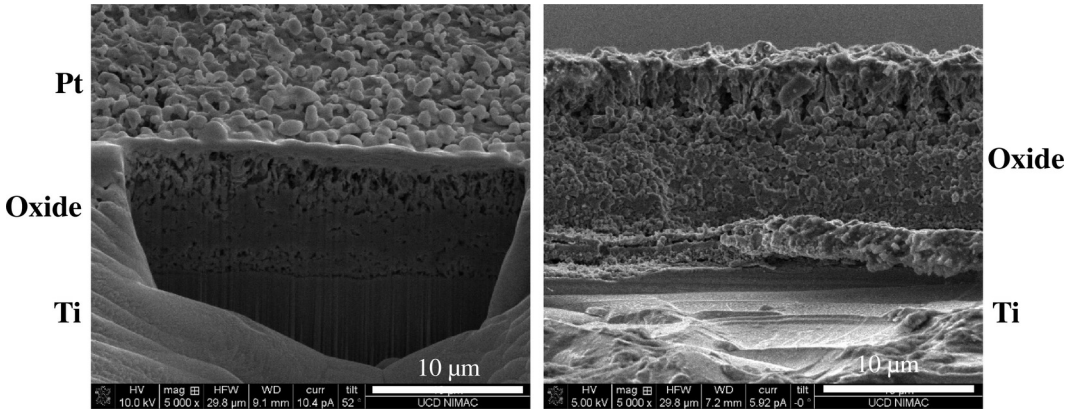

Fig. 2. SEM images of oxide cross-section prepared using the FIB (Left) and metallographic technique (Right). The images were obtained using an FEI Quanta 3D FEG DualBeam system. The average oxide-layer thickness for both techniques as measured using a Digimizer 4.0 image analysis software is 9.89 μm. (Note a 52° tilt angle is used for the FIB image).