



# Optical emission spectroscopic determination of the optimum regions for micro-arc oxidation of titanium



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## ABSTRACT

In recent years, a relatively novel anodic surface modification technique, known as micro-arc oxidation (MAO), has gained ground because of the many benefits it offers such as a low-cost manufacturing process, low environmental impact, strong film adhesion, and the feasibility for tailoring microstructures. In this study, optical emission spectroscopy (OES) was employed *in-situ* to systematically unveil how the optical-active species in the discharge manipulate the microstructure formation of the MAO layers on titanium, and hence determine the optimal operation conditions of the MAO process. Specifically, during the MAO process on titanium, we varied the applied voltage and pH value of the electrolytes, and observed the behavior of the oxide layer formation and discharge channel evolution in several stages as a function of treatment time. Based on the experiment results, current transient response, morphological observations, compositions of the formed layers, and OES spectra of optical-active species during MAO process, the phenomena and mechanisms in each MAO stage were expounded. In OES finding, specific plasma species were detected for the regular- and macular-growth modes, separately. Moreover, the *in-situ* OES spectra accurately corresponded with the results of the current transient response, specimen photographs, SEM images, XRD patterns, and composition of the obtained oxide layers. These results prove that *in-situ* OES observations can be used to successfully determine the most suitable conditions for the MAO treatment of titanium.

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## 1. Introduction

(MAO) treatment which also known as plasma electrolytic oxidation (PEO) is an advantage aqueous anodic treatment. Generally, the valve metal was put into the electrolyte as an anode, by giving relatively high polarization to trigger the arc behavior at the surface of the specimen. After the treatment, the oxide layer grows firmly on the metal surface. MAO treatment of titanium and titanium alloys has improved their biocompatibility when used for orthopedic and dental implants [1–3], their surface properties, particularly wear resistance [4], has made them potential candidates for a wide range of possible applications, such as photo-sensitive heterogeneous catalysts [5], anode layer for dye-sensitized solar cells [6], as well as anode material for secondary lithium-ion batteries [7]. The morphologies and properties of MAO layers grown on titanium are largely influenced by electrolyte composition, type of substrate, applied voltage, current density, and treatment duration [1]. Unfortunately, as opposed to other light metals and alloys, for titanium alloys, few studies have been performed on bridging the

correlation between MAO layer growth mechanism/characteristics, and plasma discharge species, where a tendency could exist in emission line and intensity changes as a function of treatment parameters.

Optical emission spectroscopy (OES), a plasma diagnostic technique, has been used to establish a possible mechanism for plasma-based vacuum depositions through *in-situ* observation of optically active species during the deposition process. The aqueous electrolyte was obstructed for OES to collect the optical signal through the medium. In Hussein's research, OES system successfully introduced with MAO process on aluminum metal to investigate the plasma electron concentrations and temperatures [8]. Furthermore, in Jovic's research, OES monitoring provided powerful evidence that plasma electron density diagnostics is performed either from the H<sub>β</sub> or non-hydrogenic ion of Al and Mg [9]. In the present study, OES characterization is possible to identify active species in the plasma discharge of MAO processes carried out in vacuum and aqueous environments. In addition, it opened the door for *in-situ* investigations on the possible mechanisms or reactions that take place during MAO process, so as to control the oxide film growth.

The research employs an OES technique, in combination with various material characterization methods, to demonstrate the phenomena of MAO treatment on titanium under various conditions: a systematical adjustment of applied voltage (450, 500 and 550 V), and various electrolyte pH values (4.7, 7.0 and 9.0). The finding revealed a better

Abbreviations: MAO, micro-arc oxidation; OES, optical emission spectroscopy; PEO, plasma electrolytic oxidation.

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understanding of underlying phenomena during MAO process on metal titanium can be obtained, as well as the capability for on-site adjustments of MAO parameters for a better process control.

## 2. Materials and methods

Fig. 1 shows a schematic representation of the experimental set-up designed for the study. Square substrates made of commercially pure titanium (ASTM CP-Ti grade II), with an area of 20 mm × 20 mm and a thickness of 1 mm, were ground with #1200 abrasive paper to obtain a surface roughness  $R_a \approx 0.02$  mm. Prior to each experimental run, the substrate, which served as the anode, was washed in an ultrasonic cleaner with acetone and distilled water sequentially. During the whole MAO process, Ti substrates were immersed thoroughly in the electrolyte. Three sets of electrolytes were prepared from 0.05 M  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ , followed by adding drop by drop of various amounts of 2.5 M NaOH solution to reach acidic (pH = 4.7), neutral (pH = 7.0), and alkaline (pH = 9.0) electrolyte baths. With their corresponding conductivity values of 5.7, 9.2, and 10.2  $\text{mS} \cdot \text{cm}^{-1}$ . The electrolyte temperature was kept at  $25 \pm 2$  °C with a coil cooling system.

A DC power supply (Kyosan Electric) with a power controller (Melec SPIK 2000A) was employed to apply a constant voltage at 450, 500, and 550 V. Based on the past research [8], Chu selected an alkaline bath (pH = 9.8) and applied voltage of 490 V to fabricate anatase on metal titanium. Moreover, in Chung's study [10], with wide range of pH value setting (pH = 4.81 to 12) associated with applied voltage range from 430 V to 480 V, the bioactive MAO layer were prepared including different crystal structure such as A-TiO<sub>2</sub>, R-TiO<sub>2</sub>, HAp, Sr-HAp, and dual-phase HAp-TiO<sub>2</sub>. In the study, author decided to investigate the effect of pH value and applied voltage to MAO process on metal titanium.

The obtained samples from MAO process were denoted as A1, A2, A3, N1, N2, N3, B1, B2 and B3, where A, N and B stand for acidic (pH = 4.7), neutral (pH = 7.0) and alkaline (pH = 9.0) electrolyte bath, respectively. While 1, 2 and 3 stand for the applied voltages of 450, 500 and 550 V, respectively.

The applied voltage and current transient response were monitored and recorded by an oscilloscope (Tektronix TDS 2022B). The micro-arc discharge emission was measured using an optical emission spectrometer (OES, BRC111A spectrometer, B&W Tek Inc.). The spectral lines in the range 200 to 800 nm in 0.8 nm steps was used to obtain the emission spectra of the discharge plasma by introducing an optical fiber into the electrolyte tank. In order to identify the elements/species associated with the micro-arc discharge, so as to understand the evolution of the oxide layer in acidic, neutral, and alkaline electrolytes.

An X-ray diffractometer (XRD, Bruker D8 HRXRD) with  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5406$  Å) was employed to determine the phase composition

of the MAO layers. To obtain the XRD patterns, each sample was scanned from 20° to 80° with a scanning rate of  $4^\circ \text{min}^{-1}$  at a grazing incident angle of 1°. The surface morphology and thickness (cross-sectional view) of the Ti-MAO layer were observed with a variable vacuum scanning electron microscope (VVSEM, Hitachi S3000-N).

## 3. Results and discussion

### 3.1. Characteristics of Ti-MAO current transient response

Fig. 2 shows the current density transient of MAO process on titanium under different parameter settings. Notice that the full test duration for sample B3 (applied 550 V in pH = 9.0 electrolyte bath) was only approximately 3 min, which was intentionally interrupted due to unexpected occurrence of turbulent arcing on the sample.

It is clearly seen that MAO processes carried out at low applied voltages, or in alkaline [8–10] electrolytes, first experienced a peak initial current transient, which decreased and remained relatively low throughout the remaining treatment time. This behavior is typically seen for most regular MAO processes, characterized as type-b systems [11].

MAO processes carried out at high applied voltages, or in alkaline electrolytes, experience a much higher (and also non-typical and complicated) current transient. These cases, of which relatively few have been reported in the literature, are referred to as type-a behavior [11]. Therefore, to illustrate the phenomena and mechanism of layer formations during the MAO process, a schematic of the J-t plot was divided into various regions, which were proposed in Fig. 2d. The current transient behavior during this type of MAO processes can be characterized as follows; During the initial step ( $t = \tau_0$ ), a maximum current density is observed due to rapid ramp-up of the input voltage, which caused intense oxygen evolution at the titanium surface. In region I ( $\tau_0 < t < \tau_1$ ), the current density decreases rapidly due to the formation of highly resistive (dielectric) oxide layers. Next, a slow increase in the current density that was shown in region II ( $\tau_1 < t < \tau_2$ ) occurs because of the massive gas liberation due to O<sub>2</sub> evolution. Consequently, the sparked ignition of region III ( $\tau_2 < t < \tau_3$ ) occurs to facilitate the rapid current density rise [11]. In region IV ( $\tau_3 < t < \tau_4$ ), the increasing MAO film thickness shifts the discharge pattern from a population of small and frequent discharge events, toward larger but scarcer events. The current density reaches a constant value in region V ( $\tau_4 < t < \tau_5$ ), where an ultimate MAO layer thickness is achieved. The events of the dielectric breakdown with associated film growth compromise with film dissolution. In the final region VI ( $t > \tau_5$ ), the slight increase of current density could be caused by the unwanted arc events over the specimen surface, the unwanted arc may damage the dielectric layer and reveal the inner

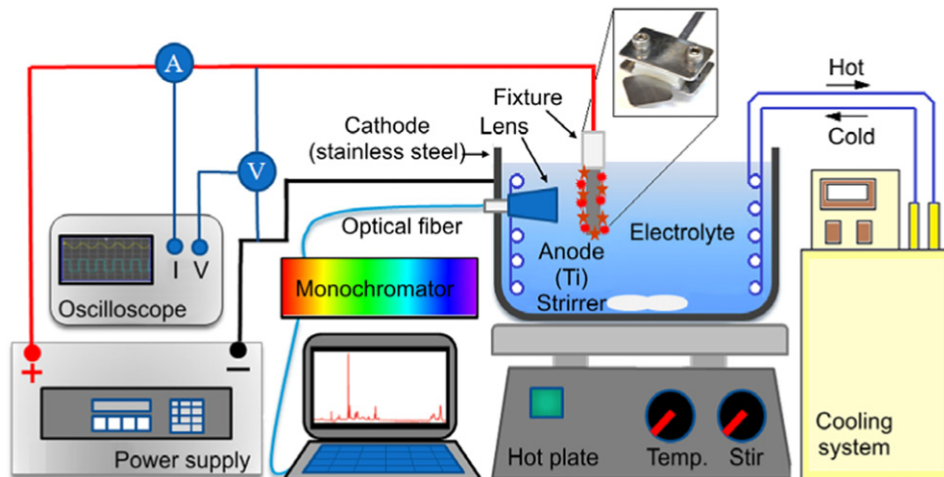


Fig. 1. Schematic diagram of the MAO process and OES system.

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