

# Effect of Electrolyte Concentration on the Surface Properties of Nanoporous TiO<sub>2</sub> Layers Formed on Micro-roughened Titanium

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**Abstract** The aim of this study was to evaluate the effect of electrolyte concentration on the surface morphology, surface topography, wettability and surface roughness of nanoporous titanium dioxide (TiO<sub>2</sub>) layers. Titanium (Ti) samples were treated by sandblasting and acid-etching processes. TiO<sub>2</sub> layers were formed on sandblasted/acid-etched titanium in electrolytes containing different HF concentration (% 0.25-2). The samples were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM) and atomic force microscopy (AFM). The surface roughness and the wettability of the samples were measured using profilometry and a contact angle measurement system. The samples, which were anodized after sandblasting/acid-etching treatment had amorphous structure and peaks from the substrate were observed. The results showed that with increasing HF concentration, the surface morphology of the samples were significantly changed. All the treated samples exhibited hydrophilic properties.

**Keywords** Nanoporous TiO<sub>2</sub> Layer, Sandblasting, Surface Morphology, Hydrophilic

## 1. Introduction

Titanium (Ti) and its alloys have been widely used as dental and orthopedic materials due to their high mechanical properties, excellent corrosion resistance and biocompatibility [1,2]. In view of exploiting specific TiO<sub>2</sub> properties, a good deal of attention has been given to applications in photovoltaic cells [3], photocatalysis [4], sensing [5], wettability-based templates [6] and biomaterials [7] due to the unique physical and chemical properties.

After the implantation, the connection begins in directly

between implant surface and bone tissues. TiO<sub>2</sub> layers of the implant influence biocompatibilities of the Ti implant. The existence of the air-formed oxides on the metal surfaces do not boost a direct chemical bond with bone tissue, therefore, surface modification, altering topography and chemical composition of these materials are required to enhance direct structural and functional anchoring of the prosthesis to the living bone (osseointegration). There are some most significant surface treatments of commercially available implants and prosthesis including: sandblasting, acid etching, plasma spraying, anodizing and micro-arc oxidation [8-13].

Recent researches have shown that nanoscale topography as well as the sequence of the nanofeatures organization is a critical factor supporting early cell responses to the implant surface [14-19]. Hereby, the fabrication of highly ordered TiO<sub>2</sub> nanotube films has attracted much attention by scientist for biomedical applications [20]. Several parameters play significant roles on changing the formation of nanoporous TiO<sub>2</sub> layer by the anodization of titanium, such as the applied voltage, electrolyte concentration, temperature of electrolyte and anodization time.

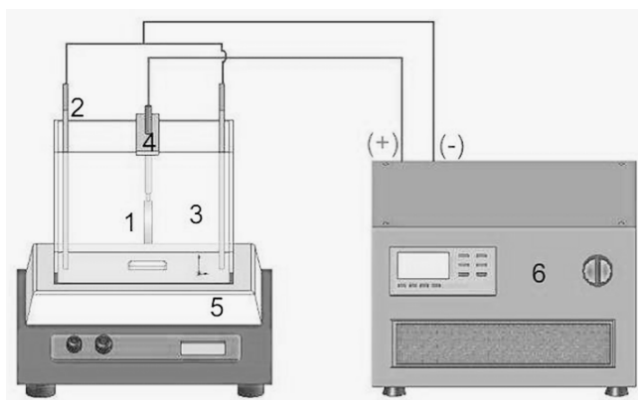
The present work investigated the surface characteristics of nanoporous TiO<sub>2</sub> layers by anodizing in various HF containing electrolytes followed by sandblasting and acid etching process. Surface morphology, topography, roughness and wettability of the prepared nanoporous TiO<sub>2</sub> layers were investigated in details.

## 2. Experimental

A commercially pure (c.p.) titanium (ASTM Grade 2) was cut into discs with a diameter of 25 mm and a thickness of 8 mm, then mechanically polished with 80-grit to 1200-grit emery paper. All specimens were sandblasted with 50 μm

alumina (Al<sub>2</sub>O<sub>3</sub>) particles and acid etched with HCl/H<sub>2</sub>SO<sub>4</sub>. After the etching process, the specimens ultrasonically cleaned with acetone for 20 min. Prior to the anodic oxidation, the samples were degreased in a mixture of nitric acid and hydrofluoric acid solutions for ten seconds to remove the air-formed oxide layer.

The schematic diagram of the anodizing system is shown in Fig. 1. Anodization was carried out in a two-electrode configuration connected to a DC power supply under a constant 20 V anodic potential at room temperature (25°C). Experiments were performed at four different electrolyte concentration (% 0.25, 0.5, 1, and 2 HF). The electrolyte was homogenized with magnetic stirring.

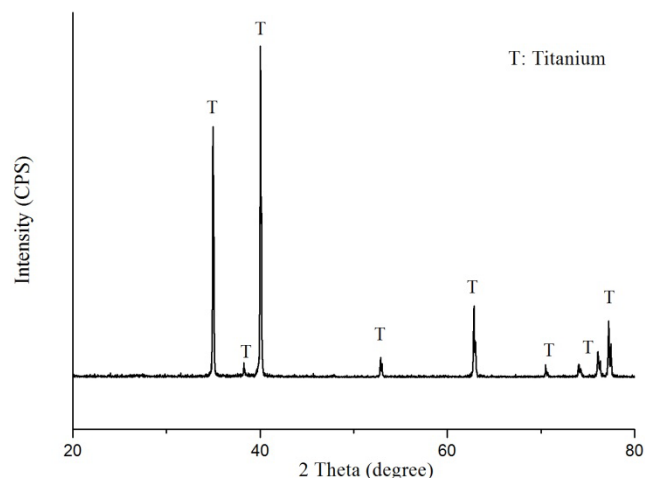


**Figure 1.** Schematic diagram of anodizing system. (1) Anode (2) Cathode (3) Electrolyte (4) Anode holder (5) Hot plate (6) Power supply.

X-ray diffraction (XRD, Thermo Scientific, ARL K<sub>α</sub>) patterns of all samples were taken to identify phase structures with the aid of an X-ray diffractometer having a CuK<sub>α</sub> characteristic radiation source. Diffraction patterns were collected in the range of 10° to 80° with a 2 theta scanning rate of 2°/min. The morphology of the anodized titanium was analyzed using a scanning electron microscope (SEM, JEOL 6060) and an atomic force microscope (AFM, EasyScan2, Nanosurf). The surface roughness was measured with surface profilometer (Ambios Technology XP-2). The surface wettability was tested by contact angle (Izmir Katip Celebi University-Turkey) in triple for each sample.

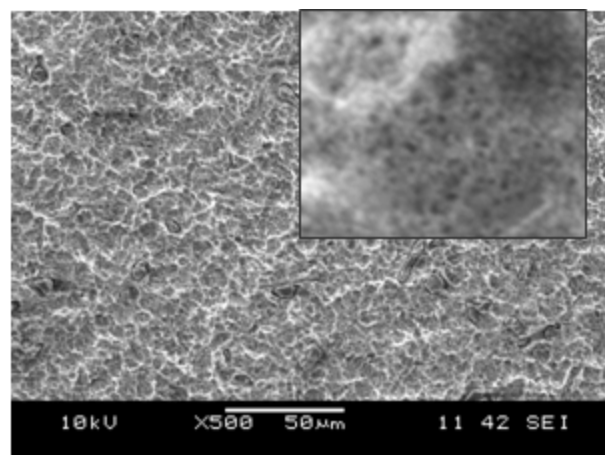
### 3. Results and Discussion

Fig. 2 depicts the XRD pattern of all treated samples after the anodization. All samples demonstrated the same XRD patterns which are amorphous. There are no peaks of other phases observed in the XRD pattern. Furthermore, they can be converted to an anatase or rutile crystalline phases form under suitable heat treatment [21].

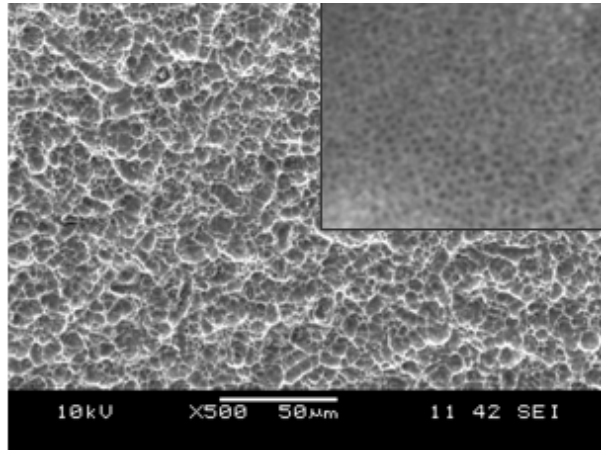


**Figure 2.** XRD patterns of anodized sample.

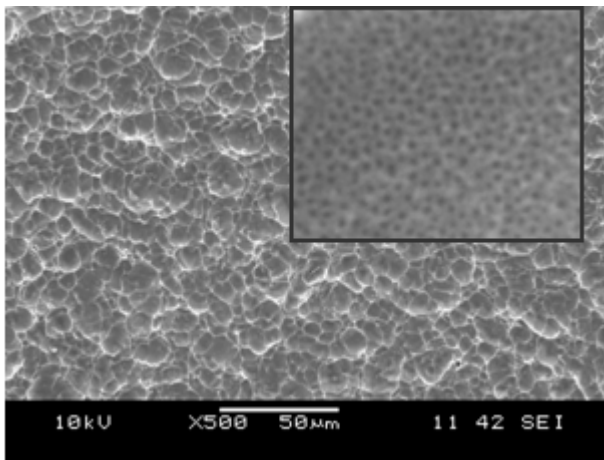
Fig. 3 shows SEM images of the surface morphologies of TiO<sub>2</sub> layers that derived from after the anodization of sandblasting and etching applied to Ti samples at various HF concentrations. It was noticed that the presence of the sand granules were observed at low HF concentration. It is well known that formation of nanopores mechanism is a competition between etching and anodizing processes. Within this framework, it can be mentioned that the acidic dissolution is not sufficient. It was observed that these kinds of contaminations were removed on the surface with increasing HF concentration. Moreover, it was obtained that the size of pits gradually raised and formation of the nanopores became clearer on the surface with increasing HF concentration. In this study, TiO<sub>2</sub> nanopores of about 250 nm long, with 10 to 30 nm vessel wall thickness and inner diameters ranging from 40 to 80 nm were obtained by means of high-resolution images of SEM.



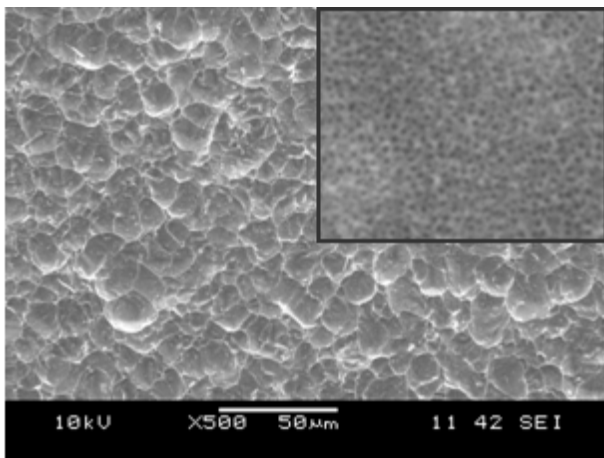
a



b



c

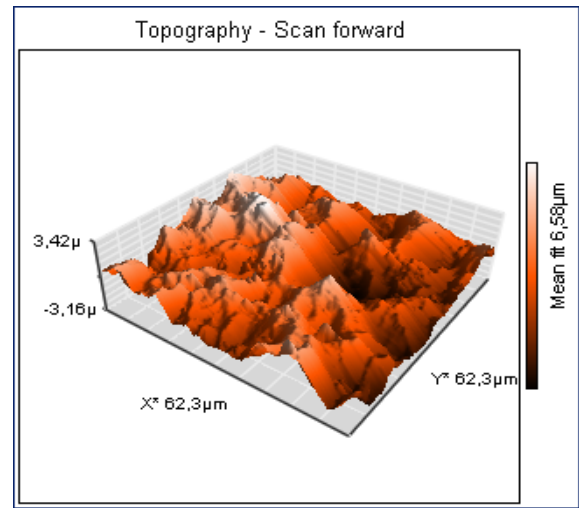


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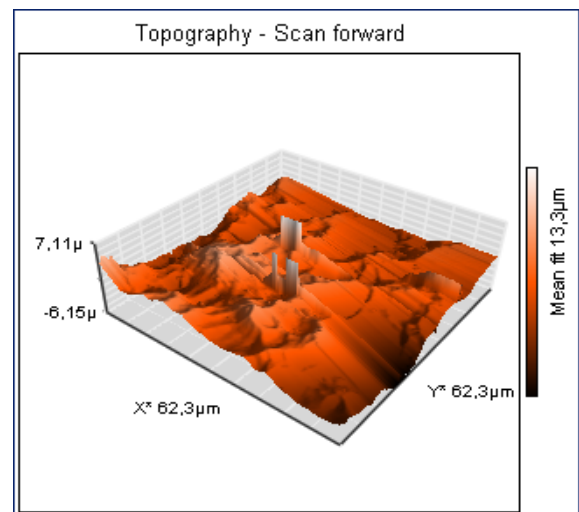
**Figure 3.** SEM micrographs of the nano-porous TiO<sub>2</sub> layers anodized in (a) 0.25 wt.% HF (b) 0.50 wt.% HF (c) 1 wt.% HF (d) 2 wt.% HF

Fig. 4 illustrates the surface topographies of nanoporous TiO<sub>2</sub> layer after the anodization of sanding and etching applied to Ti samples at various HF concentrations. Similar to surface morphologies, dimension of micro pits took place to expand on the surface with increasing HF concentration. After the anodization, the voids formed in the range of approximately 20-30 µm in the electrolyte containing 0.2%

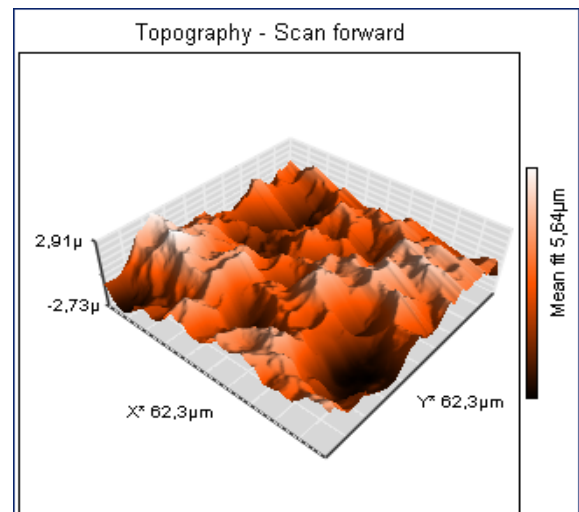
HF, whereas there was denser and more compact topography on the surface in the electrolyte containing 0.25 % HF. It can be attributed to the intensity of the acidic dissolution.



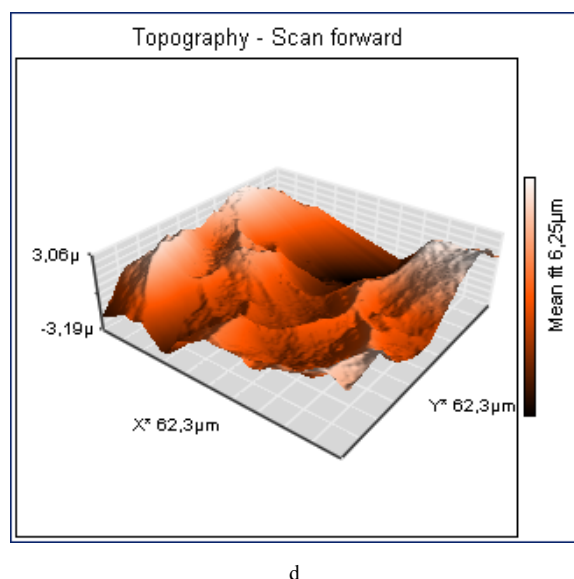
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**Figure 4.** AFM micrographs of the nano-porous TiO<sub>2</sub> layers anodized in (a) 0.25 wt.% HF (b) 0.50 wt.% HF (c) 1 wt.% HF (d) 2 wt.% HF

**Table 1.** Surface roughness and wettability of the samples

Electrolyte Concentration (% HF)	Surface roughness parameters			Contact angle (°)
	Ra (μm)	Rt (μm)	Rq (μm)	
0.25	1.62	10.64	2.01	7.50
0.50	1.44	8.47	1.78	17.45
1.00	1.29	8.55	1.61	4,23
2.00	1.03	8.82	1.30	58.51

It is well known that surface roughness is one of the most important parameter for the biomechanical anchoring between the bones and Ti implant after the implantation process. In the same way, wettability ensures rapid osseointegration. As a result of this, rapid osseointegration plays important roles on the healing time. The surface roughness and contact angle values were measured after the anodization of the sanding and etching applied to Ti samples. Surface roughness gradually decreased with the increasing HF concentration. As can be seen in surface topographies, diameter of microvoids of TiO<sub>2</sub> layers increases, whereas dense of microvoids decrease by with increasing of HF concentration. The values of the contact angle indicate whether the surface is hydrophilic or hydrophobic. The surface wettability is generally determined by the water contact angle. The key factors that affect the contact angle are surface chemical composition and surface texture [22]. When the contact angle was taken into consideration, it was obtained that the surfaces of the all samples exhibited hydrophilic character. The lowest contact angle value was observed on the anodized sample in the electrolyte containing 1 % HF.

## 4. Conclusions

Finally, the titanium samples were sandblasted and acid

etched follow by anodizing in different HF concentration. After anodization process, micro and nano structures were produced on the samples. As a result of the anodization, different surface morphologies formed that were first time. It was observed that surface morphologies of the TiO<sub>2</sub> layers changed with increasing electrolytic concentration and the roughness of the surfaces increased. This study indicated that the nanoporous TiO<sub>2</sub> layers formed on micro-roughened titanium surfaces exhibited lower contact angle.

Desired implant surface properties were obtained in terms of surface roughness and contact angle values.

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