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Scanning Electron Microscope for Characterising of Micro- and Nanostructured Titanium Surfaces

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1. Introduction

Titanium and its alloys have been used broadly and successfully for numerous applications such as sport equipment [1], aerospace industry [2], marine application [3], medical applications [4] because of its optimum mechanical properties, outstanding corrosion resistance and bio-inert due to the presence of a thin layer of titanium oxide which a naturally formed onto the titanium surface [5-6]. This layer mainly consists of titanium dioxide or titania. Properties of oxide films covering titanium implant surfaces are a key role for a successful osseointegration [7-8], wear and corrosion resistance [9]. Moreover, titania has a large number of potentials in water photoelectrolysis and photocatalysis [10], sensors [11], wastewater remediation [12], automotive industry [13], industrial applications [14] and micro-optoelectronic applications [15]. However, there are some disadvantages of the native titanium oxide which has poor mechanical properties and easily fractured under small scale of fretting and wears conditions [16]. Therefore, many surface modification treatments for examples anodisation (anodic oxidation), cathodic electrodeposition and sol-gel reactions [17-22] have been studied in order to improve the performance of titanium. Moreover, surface properties such as topography, chemical composition and hydrophilicity have an effect on the mechanical stability of the implant-tissue interface. Various surface modification methods of titanium have been shown to improve interfacial interactions at the bone-implant interface and their clinical performance. Moreover, the biological performance of implantable titanium depends crucially on their surface topography in the micrometre (structures larger than 1 micron) and nanometre (structures smaller than 1 micron) range. Surface micro- and nano-topography can reduced inflammatory and guide direct osteoblast responses by altering adhesion, recruitment, movement, morphology, apoptosis and gene expression, and subsequently protein production [23-25]. An anodisation is a simple and an inexpensive technique to prepare thin film titania on titanium surface in different conditions and electrolytes such as acidic, basic, neutral, organic and inorganic which affect surface architecture and chemical composition [26-27]. Anodised oxide layer has thickness in the range of 20 to 180 nm which is thicker than a naturally formed oxide [28]. Moreover, this technique is presently used to achieve micro- and nano-topography surfaces. An anodisation is an electrolytic etching for coating the surface of a metal with an oxide layer which changes the microscopic texture of the surface and the crystal structure of the metal

near the surface. An anodisation process accelerates the formation of an oxide coating under controlled conditions to provide the desired result. Since the coating is biocompatible as well as nontoxic, the process lends itself to achieve drastic improvement in implant performance. By adjusting the anodisation condition such as electrolyte, pH, voltage and time, micro- and nano-scale properties could be controlled.

In this article, the morphological of surface was studied by means of scanning electron microscope (SEM) after surface modification in order to evaluate qualitatively the effect of the anodisation conditions. For this purpose, the SEM uses to examine morphological of development of anodised film of titanium that were prepared under different controlled conditions.

2. Materials and methods

2.1 Preparation of surface

Prior to anodisation, commercially pure titanium grade 2 were provided by Prolog Titanium Co., Ltd and cut into 1 cm × 1 cm squares. Titanium sheets were abraded mechanically using silicon carbide (SiC) abrasive papers (Buehler) number 120 to 2000 and rinsed with distilled water. The surface of sheets were sequentially polished to a mirror finished with aqueous alumina (Al₂O₃) 5, 1, 0.3 and 0.05 micron (Buehler, Alpha Micropolish II). Afterward clean with acetone in ultrasonic bath.

2.2 Remove oxide

Titanium surfaces were immersed in an acid mixture (2 ml 48% HF (48% in water) which purchased from Panreac + 3 ml 70% HNO₃ (70% in water) which purchased from Fluka + 100 ml DI water) about 90 seconds to remove the naturally formed oxide layer and then immediately treated by anodisation. All electrolytes were prepared with reagent grade chemicals.

2.3 Anodisation

The electrochemical cell consists of a two electrodes system which graphite acting as the counter electrode (cathode) and titanium sheet acting as the working electrode (anode). The anode and cathode were connected by copper wires and were linked to a positive and negative port of a DC power supply (KMB 3002), respectively. During processing, the anode and cathode were kept parallel with a separation distance of about 1 cm, and were immersed into an electrolyte. Anodisation was performed under potentiostatic conditions at 20 volts. All experiments were carried out at room temperature. Test conditions applied vary in terms of the concentration of acetic acid, the concentration of hydrofluoric acid and an anodisation time. Different series of experiments have been performed by changing the associated experimental parameters as shown in Table 1. After the electrochemical process, the titanium sheets were immediately rinsed by deionised water and heated at 120°C for 30 minutes.

2.4 Surface characterisation

The surface morphology of the samples was observed by using Scanning electron microscope (SEM: JEOL 6300) with Dispersive X-Ray Spectroscopy (EDS) technique.

	Acetic concentration (M)	Hydrofluoric acid (wt%)	Anodising time (minutes)
Series 1	0.001, 0.01, 0.1, 1 and 10M	-	120
Series 2	1 M	-	30, 60, 120, 240, 360 and 480
Series 3	1 M	0.075	30, 60, 360, 480, 720, 1440, 2160 and 2880
Series 4	1 M	0.5, 1.5 and 2.0	60

Table 1. Parameters used for anodisation

3. Result and discussion

In order to find out the effect of anodisation electrolyte and anodisation time on the forming of the oxide at constant voltage in an ambient temperature; the structure of morphology were investigated. Experimental with different anodisation conditions: the concentration of acetic acid, the concentration of hydrofluoric acid and an anodisation time were lead to get an overall view of the formation process of titania nanotubes.

3.1 Effect of concentration of acetic acid on the surface topography

Figure 1 displayed scanning electron microscope (SEM) photographs of an untreated and the anodised titanium surface at 20 volts in different electrolytes concentration. An untreated sample has no visible scratches or wrinkles (figure 1a). The effect of concentration of electrolytes on the surface morphology of the anodic oxide film formed on titanium was monitored. Based on the experimental observation, it was showed that the passive film formed on titanium surface in low concentrations of acetic acid range which from 0.001 to 0.1 M (figure 1(b-d)). The flower-like structures [29] were visible on the substrates which anodised in 1 M acetic acid. Moreover, upon increase concentration of acetic acid the surface morphologies shown the concentration of the flower was developed and increased as shown in figure 1e - 1f. The average diameter of the flowers formed in an acetic acid for 120 minutes was around 300 nanometres.

3.2 Effect of anodisation time on the surface topography

The effect of anodisation time on the morphology of an oxide film in 1M acetic acid was investigated. Figure 2(b-g) summarised the effect of anodisation time on the development of an anodised film in 1M acetic acid at 20 volts. Within 30 minutes (figure 2b), SEM image revealed the formation of a continuous of oxide film over the surface. Flower-like structures were developed at 60 minutes (figure 2c). The density of the flower oxides was observed with the increasing of anodisation time. The average diameter of the flowers increases from a few hundred nanometres to 1200 nanometres.

The effect of hydrofluoric acid and anodisation time on the formation of titania nanotubes in 1M acetic acid with 0.075 wt% HF is studied. SEM image of the surface morphologies obtained in 1 M acetic acid with 0.075 %wt HF at different anodisation time are shown in figure 3(b-i).

The results demonstrated at the initial stage of anodisation (Figure 3(b-c)), the tube-like features appeared over the titanium surface. For longer anodisation time, it can be seen from figure 3(e-f) that the architecture transformation from tube-like nanostructure to a sponge-like titania film with nanoholes. Further anodisation time, the surface of nanoholes is covered with the oxide film (figure 3(g-h)). When the anodisation time is prolonged to 2880 minutes, the discontinuous oxide film covered the titanium surface. The results confirm that fluorine containing electrolyte is a capable electrolyte for anodic formation of titania nanotubes.

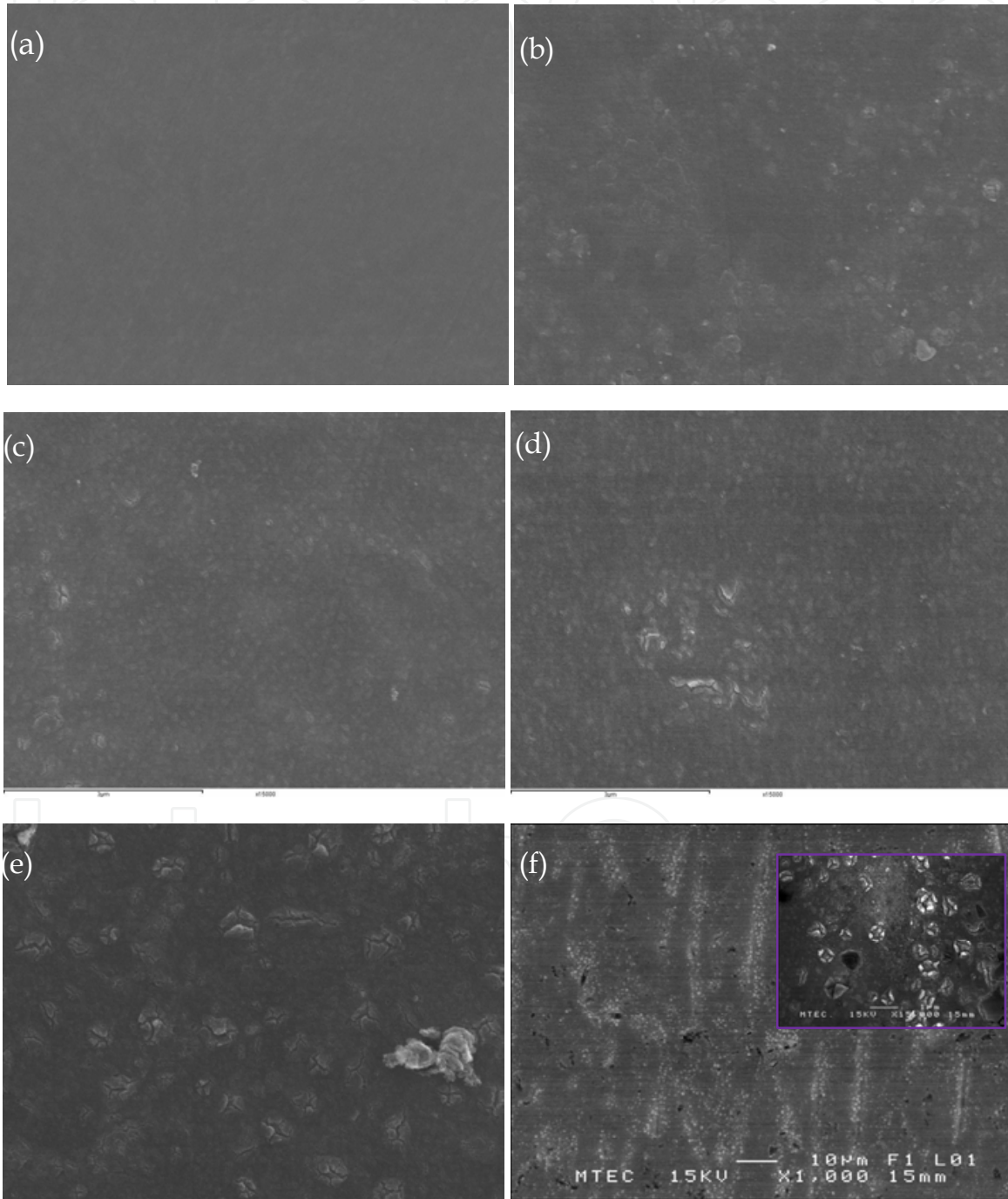


Fig. 1. SEM images of titanium sheets (a) untreated surface and anodised in (b) 0.001 (c) 0.01 (d) 0.1 (e) 1 and (f) 10M acetic acid at 20 volts for 120 minutes at room temperature.

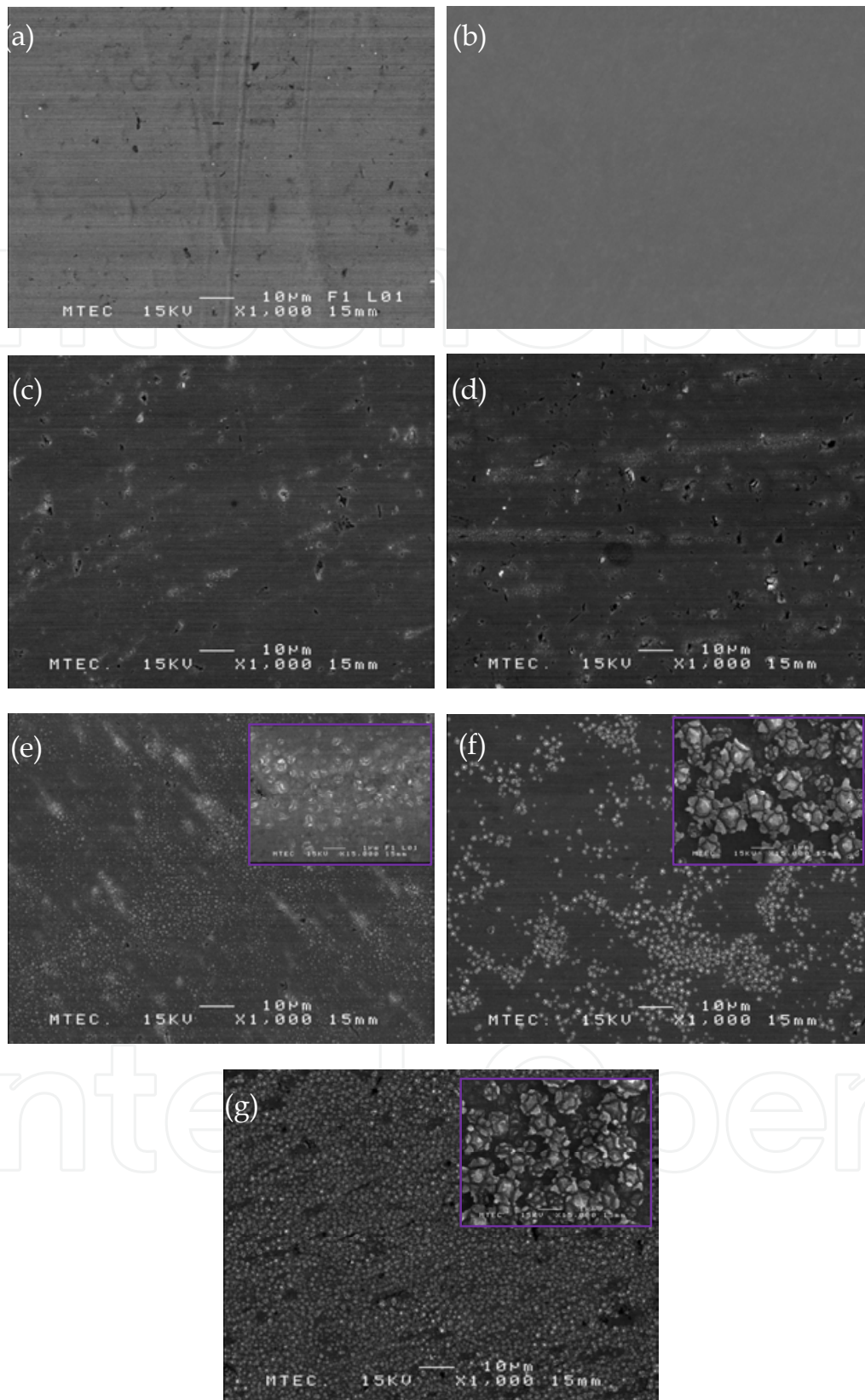
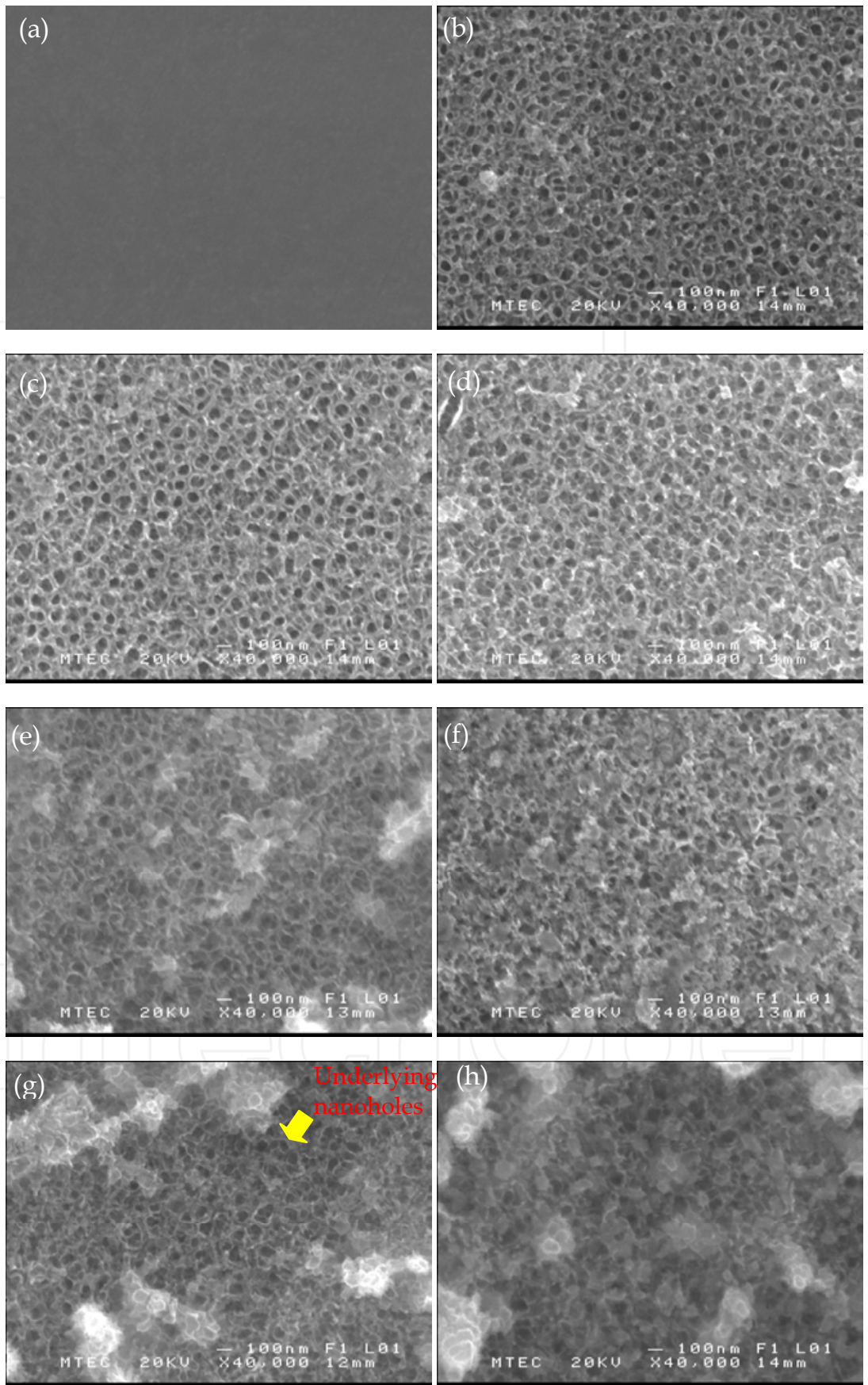


Fig. 2. SEM images of titanium sheets (a) untreated surface and anodised in 1M acetic acid at 20 volts for (b) 30 minutes (c) 60 minutes (d) 120 minutes (e) 240 minutes (f) 360 minutes and (g) 480 minutes at room temperature.



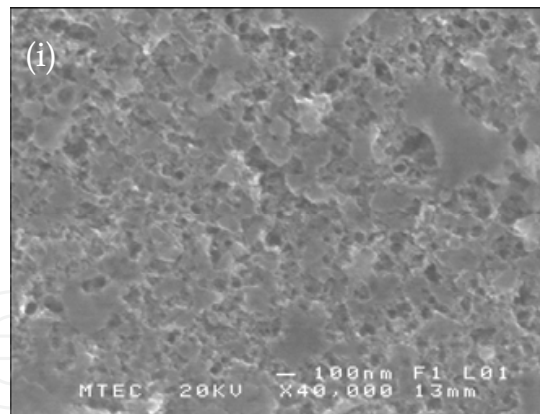


Fig. 3. SEM images of titanium sheets (a) untreated surface and anodised in 1M acetic acid with 0.075 wt% HF at 20 volts for (b) 30 minutes (c) 60 minutes (d) 360 minutes (e) 480 minutes (f) 720 minutes (g) 1440 minutes (h) 2160 minutes and (i) 2880 minutes at room temperature.

3.3 Effect of concentration of hydrofluoric acid on the surface topography

The surface topologies of titanium sheets anodised in electrolyte containing 0.1 M acetic acid with different concentration of HF: 0.075, 0.5, 1.5 and 2.0 wt% are shown in Figure 4. The anodisation was carried out at 20 volts. A network structure appears on the anodised titanium surfaces with concentration of 0.075 wt% HF (Figure 4b). Anodisation in 0.5 wt% and 1.5 wt% HF containing occur a highly ordered and uniform titanium oxide nanotube arrays (Figure 4 (d-e)). The average nanotube inner diameter is approximately 74.5 and 76.5 nanometre, respectively. As the concentration of hydrofluoric concentration was further increased to 2.0 wt%, the surface architecture developed sponge-like (Figure 4f). It points out that the concentration of hydrofluoric acid affect the morphology of titanium surface.

The anodic growth of compact oxides on titanium substrate and the formation of nanotubes in fluoride-containing electrolytes is the result of key processes [30] which are (1) Field-assisted oxidation of the titanium metal that leads to oxide growth at the surface due to interaction of titanium with O^{2-} or OH^- ions. An initial oxide layer formed on the substrate, these anions travel through the oxide layer reaching the titanium/oxide interface. (2) Titanium metal ion (Ti^{4+}) migrate from the substrate at the titanium/oxide interface; Ti^{4+} cations will ejected from the titanium/oxide interface under application of an electric field that move towards the oxide/electrolyte interface. (3) Field-assisted dissolution of titanium metal ion at the oxide/electrolyte interface into the electrolyte. (4) Chemical dissolution of titanium metal ion and TiO_2 due to etching away by fluoride ions. The reactions are [31]:

at anode:

1. oxidation of titanium metal which releases titanium metal ions (Ti^{4+}) and electron



2. interaction of titanium metal ions with O^{2-} or OH^- ions





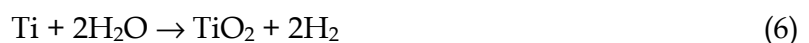
Equation (2) and (3) elucidate the hydrated anodic layer and the oxide layer. Further oxide is produced when the hydrated anodic layer releases water by a condensation reaction as the following equation:



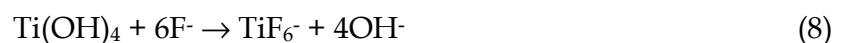
at cathode:



The overall process for anodic oxidation of titanium can be represented as:



In the presence of fluoride ions electrolyte, fluoride ions enters the $\text{Ti}(\text{OH})_4$ or anodic titanium oxide as the following equation:



Equation (7-8) is the mechanism of the pit formation due to the localised dissolution of the oxide and hydrated anodic layer. Then these pits transfer to bigger pores and the pore density increases subsequent to uniformly pores over the titanium surface, with the TiO_2 pores growing more and more deeply into the titanium metal. As described above, the formation of nanotubes govern by a competition between anodic oxidation and chemical dissolution of the oxide as soluble fluoride complexes.

The concentration of the HF added to the electrolyte was varied from 0.075 to 2.0 wt%. As a result, a large change in surface architecture was observed. An average diameter of the nanotubes increased as the fluoride content in electrolyte. As mentioned above, the formation of titania nanotubes determined by the oxide growth rate and the dissolution rate. A result shows that with 0.5 and 1.5 wt% HF, the dissolution rate was slow and resulted in small pore size. With increasing the concentration of HF, the dissolution rate increased and resulted in big pore. It is obvious that the dissolution rate was extremely high with 2 wt% HF because the morphology is not uniform.

The result of the chemical analysis by Energy Dispersive X-ray spectroscopy (EDS) indicated that anodised titanium in 1 M acetic acid with 0.075 wt% HF for 60 minutes at room temperature titania film are shown in figure 5b. The EDS measurements present an oxygen and titanium proportion of 34.914% and 65.086 %, respectively. The result reviewed that the chemical composition of anodic film was nonstoichiometric and the atomic ration of Ti/O is approximately 1.86. The presented of nonstoichiometric structure on the substrate layer implied that some defect exist in TiO_2 nanotubes due to oxygen deficiencies which can cause the formation of crystallographic shear planes and active Ti-sites for the adsorption and chemisorptions of OH groups or other contaminants [32].

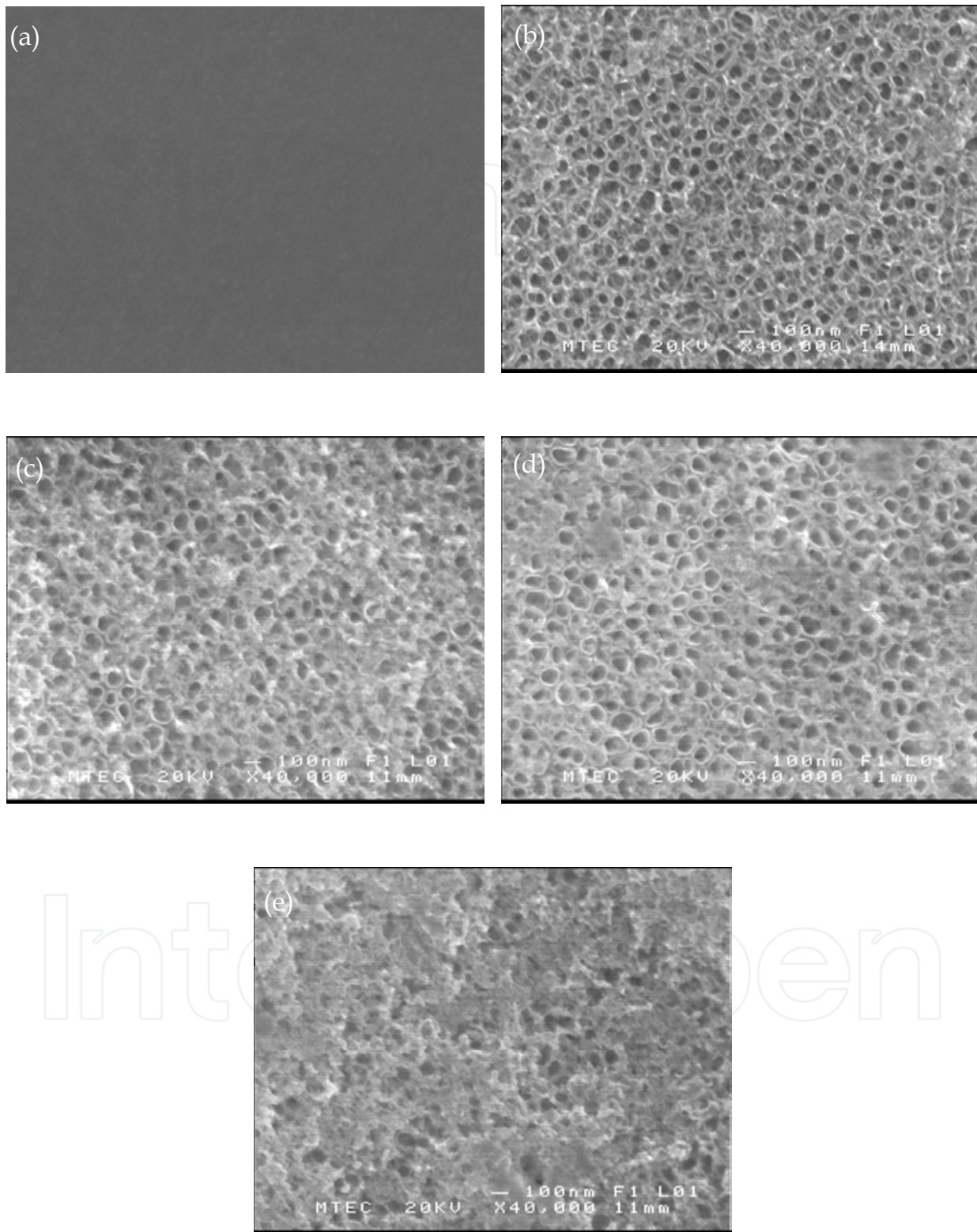


Fig. 4. SEM images of titanium sheets (a) untreated surface and anodised in 1 M acetic acid with (b) 0.075 wt% HF (c) 0.5 wt% HF (d) 1.5 wt% HF (e) 2.0 wt% HF for 60 minutes at room temperature.

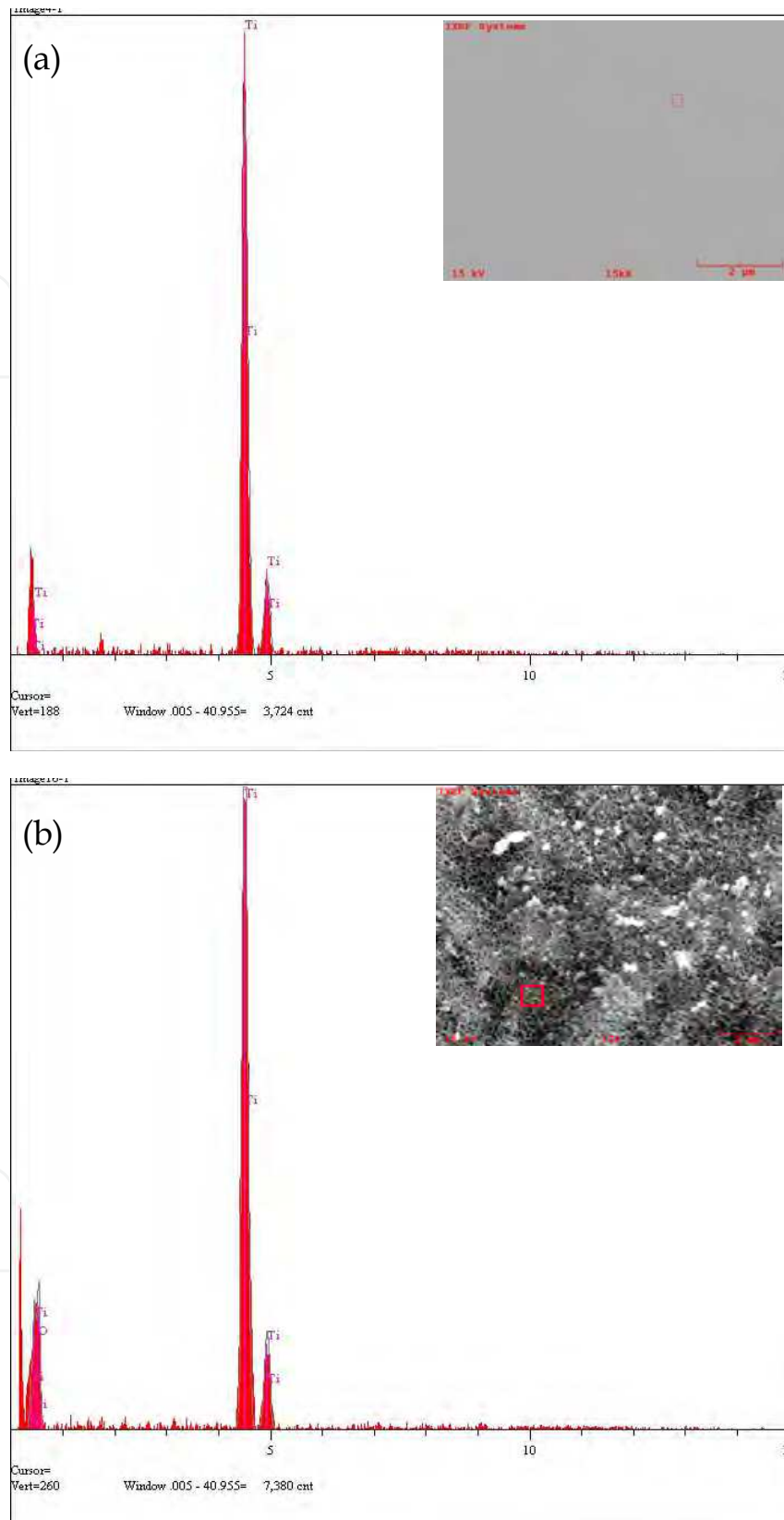


Fig. 5. SEM image of (a) untreated surface and (b) anodised in 1 M acetic acid with 0.075 wt% HF for 60 minutes at room temperature then EDS analysis of the surfaces for energy dispersive analysis was 15 kV, Takeoff Angle 35.0° and Elapsed Livetime 10.0.

4. Conclusion

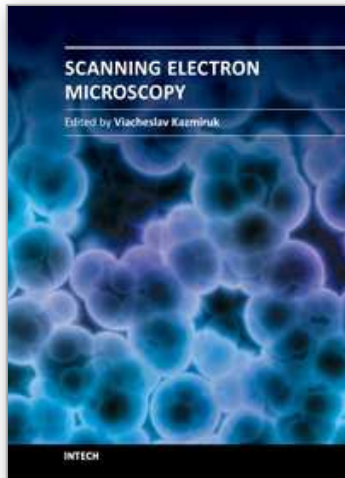
SEM analysis can clearly showed that anodisation is a simple and economical method to synthesise various surface patterns and textures on the surface of a metallic titanium surface. Moreover, surface morphology is strongly affected by anodisation condition. SEM revealed that the anodisation condition caused micro- and nanomorphological alterations of titanium surface, whereas prolonged exposure to electrolyte resulted in micromorphological changes of the titanium surface. The above result clearly point out that the hydrofluoric acid play important role in controlling the formation of titania nanotubes. Moreover, by adding fluoride ions into the electrolyte, nanotubes can be fabricated under suitable conditions

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Today, an individual would be hard-pressed to find any science field that does not employ methods and instruments based on the use of fine focused electron and ion beams. Well instrumented and supplemented with advanced methods and techniques, SEMs provide possibilities not only of surface imaging but quantitative measurement of object topologies, local electrophysical characteristics of semiconductor structures and performing elemental analysis. Moreover, a fine focused e-beam is widely used for the creation of micro and nanostructures. The book's approach covers both theoretical and practical issues related to scanning electron microscopy. The book has 41 chapters, divided into six sections: Instrumentation, Methodology, Biology, Medicine, Material Science, Nanostructured Materials for Electronic Industry, Thin Films, Membranes, Ceramic, Geoscience, and Mineralogy. Each chapter, written by different authors, is a complete work which presupposes that readers have some background knowledge on the subject.

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