EFFECTS OF ANODIZING PARAMETERS ON THE FORMATION OF TITANIUM DIOXIDE NANOTUBE ARRAYS ON Ti6Al4V ALLOY

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ABSTRACT

EFFECTS OF ANODIZING PARAMETERS ON THE FORMATION OF TITANIUM DIOXIDE NANOTUBE ARRAYS ON Ti6Al4V ALLOY

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Titanium dioxide thin films with nanoporous structures recently gained great interest due to their large surface area and high reactivity properties in their applications. One of the methods used to form titanium dioxide nanostructures is anodizing the surface of titanium and its alloys in F- ion containing electrolytes. Effects of hydrofluoric acid (HF) concentration (0.1 to 0.5 wt.%), anodizing potential (10 to 30 V) and time (30 to 180 minutes) on the titanium dioxide nanotube formation were investigated by anodically oxidizing Ti6Al4V alloy in this study. Scanning electron microscopy (SEM) images were used to detect and monitor the impact of different experimental conditions. In addition, photovoltaic effects from a well-defined cell were used to infer comparative information on the total surface area of nanotubes. The results indicated insignificant effects of HF concentration and anodizing duration on nanotube diameters but direct proportionality to anodizing potential.

Keywords: Titanium Dioxide Nanotubes, Anodic Oxidation, Nanotube Diameter

ÖΖ

Ti6AI4V ALAŞIMI ÜZERİNDE ANODİK OKSİTLEME YÖNTEMİ İLE OLUŞTURULAN TİTANİYUM OKSİT NANOTÜPLERİNİ ETKİLEYEN OKSİTLEME DEĞİŞKENLERİ

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Nanogözenekli yapıya sahip titanyum oksit ince filmler oldukça yüksek yüzey alanına sahip olmaları ve yüksek reaksiyona girebilme yetenekleri sayesinde büyük ilgi çeken bir araştırma konusudur. Titanyum oksit nanotüp oluşturma yöntemlerinden biri F- iyonu içeren elektrolit kullanarak yapılan anodik oksitlemedir. Bu çalışmada Ti6Al4V alaşımı üzerinde titanyum oksit nanotüp ince film oluşumundaki HF konsantrasyonunun (0,1 ile 0,5 ağırlıkça %), anodik potansiyelin (10 ile 30 V) ve zamanın (30 ile 180 dakika) etkileri incelenmiştir. Deney koşullarının etkileri taramalı elektron mikroskop görüntüleri ile değerlendirilmiştir. Ek olarak, nanotüplerin toplam yüzey alanın birbiri ile kıyaslanması için, üretilen ince filmlerin fotoelektrik özellikleri incelenmiştir. Sonuçlar, HF konsentrasyonunun ve anodik oksitleme süresinin oluşan TiO₂ nanotüp çaplarına önemli etkisinin olmadığını ve oksitleme potansiyelinin oluşturulan TiO₂

Anahtar Kelimeler: Titanyum Oksit, Titanyum Oksit Nanotüp, Anodik Oksitleme

To My Parents

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CHAPTER 1

INTRODUCTION

Structural size reduction to the nanometer rescale causes increment of materials and methods which have unrivaled physical and chemical properties in many scope of science and technology [1, 2]. Nanostructured metal oxide materials of different physical and chemical properties have been used in dye-sensitized solar cells [3], water electrolysis [4], and photocatalysis [5]. These applications are environmentally friendly where sunlight is converted to electricity, solar energy, chemical fuel (hydrogen) and organic pollutants are degraded to harmless species.

There are various kind of oxide nanotube formation. TiO₂ nanotube structure can be achieved by three main fabrication routes namely; template method, hydrothermal method and electrochemical anodization method [6]. Several investigations involving carbon nanotube formation took place after 1990. As previously mentioned template type of nanotube formation was conducted at 1996 and hydrothermal approach of oxide nanotube formation was investigated after than other formation techniques. Until 1999 nanotube formation by anodization is not investigated. The first electrochemical generation of self-organized oxide nanotubes by anodization was informed in 1999 [7]. A timeline describing the development of nanotubular structures is shown in Figure 1.1.

In anodization of titanium, a sufficient potential is applied between a anode and a cathode in F^- containing aqueous electrolyte. After electrical potential applied, compact titanium dioxide layer on the surface of the anode took place immediately.



Figure 1.1 A simplified timeline describing the development of metal oxide nanotube synthesis techniques [8].

After initiation, which means compact oxide layer formation at the surface of the base material, ion migration figure out increase of the thickness of the oxide layer. The expansion of anodic oxide portion is resolved by the field-aided transport of mobile ions through the oxide layer. Depending on the migration rate of the involved ionic species, the growth of new oxide either proceeds at the metal/oxide or oxide/electrolyte interface. In the presence of F- ion in the electrolyte, Ti4+ and F- ions form a water soluble hexafluorotitanate $(TiF_6)^{2-}$ species according to equation (1.1).

$$TiO_2 + 6F^- + 4H^+ \rightarrow TiF_6^{2-} + 2H_2O$$
 [9] (1.1)

Porous titanium dioxide growth mechanism causes a competition between dissolution and formation of oxide layers. This oxide layers leads to a regular columnar structure growth of TiO_2 film until the steady state condition is achieved.

Generally, the pore or tube radius of Ti metallic substrate systems are known as directly proportional to the applied anodic potential. In addition, it is claimed that the effect of fluoride ion amount in the electrolyte on tube and pore geometry is minor and almost no dimensional change observed [7].

Anodizing duration is an important factor for the formation of nanotubes and TiF_6^{2-} water soluble ion. Previous investigations showed that, nanotube formation was not detected within 30 min. anodizing duration in F⁻ containing electrolytes [8-10]. For longer anodization processes, there is no limiting time for the growth of nanotubes

reported in literature. A 24 h. anodizing duration without retrogradation in nanotubes was reported [8].

At low anodizing voltages like 3 V and in only HF (balance water) containing electrolytes, etching and pore formation occurred on the surface of titanium. Up to 20 V anodic oxidation potential nanotube structure formation occurs. However, when potential increase from 20 V, titanium dioxide nanotube layer stars to dissolved. Dissolution of oxide layer cause thinning and disappearance of formed nanotube structure. [10].

Among titanium alloys, Ti6Al4V is investigated extensively due to its biocompatibility. A wide range of nanostructured materials are being used in biological applications, to enhance the growth of tissues or stop infection. However, most of the studies on TiO₂ nanotube formation involved the use of pure Ti substrates [1, 3, 7, 8 – 11]. Information on anodic oxidation of Ti6Al4V alloy is very limited and uses high concentration HF electrolytes without H₂SO₄ [6, 10]. Therefore, titanium dioxide nanotube growth on Ti6Al4V alloy by anodizing in low concentration HF electrolytes in the presence of H₂SO₄ was investigated in this study. The aim of this study was to investigate the effects of the anodizing potential, duration and HF addition to 1 M H₂SO₄ containing electrolyte on the titanium dioxide nanotube diameter and obtain comparative information for the surface areas of the oxide nanotubes by photovoltaic measurements.

CHAPTER 2

LITERATURE REVIEW

In this chapter, anodization definition, its mechanism, specific reaction of TiO_2 anodization, nanotube formation mechanism, the parameters that effects the formation of TiO_2 nanotubes and their diameters, thicknesses and electrical properties of TiO_2 nanotubes will be given. In addition, its applications and photoelectrical behavior of the TiO_2 were briefly mentioned to enlighten the purpose of the investigation of the effects of anodizing parameters on the formation of titanium dioxide nanotube arrays on Ti6Al4V alloy.

2.1 Anodization

Anodization is an electrochemical passivation procedure, which makes increment of naturally formed oxide layer thickness of the metals. The process performed in the existence of an electrical circuit where the metal part treated forms the anode. Anodizing is a widely used process in industry to increase the corrosion resistance and wear resistance of metals. Anodized parts are painted easier than bare metals. Anodic films mostly applied to aluminum alloys. Anodically oxidized films on the surface of the metals are stronger and more attached than other coating, plantings and paints [11].

Anodization is a very useful technique to form stable, protective and dense oxide layer on Al, Fe, Ti or Zr kind of valve metals and their alloys. During anodization process ion migration occurs through the solid films promoted by an electric field. Electrochemical method is preferred to be used for the highly ordered parallel porous oxide morphology or ordered pure of oxide nanotubes [12].

2.2 Anodizing Mechanism

Electrochemical anodization method of transition metals to form congruently coarse oxide layers has been full filed for many decades. Self-organized oxide nanotube layer or ordered nanopore assemblies have been studied only recently [7]. Most valve metals have naturally formed oxide layer at microscopic level. Anodization under high field mechanism leads to increase the thickness of oxide layer. There are mainly four different oxide morphologies that can be obtained by anodization process as shown in Figure 2.1.



Figure 2.1 Morphologies of oxides which can be obtained by electrochemical anodization of metallic titanium (a) a compact oxide film, (b) a disordered nanoporous layer, (c) a self-ordered nanoporous or (d) a self-ordered nanotube layer [6].

During formation of thick metal oxide, water containing electrolyte ionize to H^+ and O^{2-} while metal is oxidized (from M^0 to M^{X+}) at the metal oxide interface. The ionized metal ions (M^{X+}) migrate outwards under the applied field. O^{2-} ions move toward the metal oxide interface. In this mechanism, transfer numbers of O^{2-} and metal ions determine the growth of the oxide layers both at the outer and the inner oxide interfaces. This process is self-limiting under constant applied voltage because

increment in the oxide layer is decreased as the oxide layers become thicker. Minimization of field strength guide to the increment of oxide layer. The thickness of the oxide nanotube is reported to be proportional to the applied potential.

The most common metal for the self-ordering porous valve metal anodization is aluminum. Highly ordered porous Al_2O_3 layers thickness are increased anodically on Al surfaces. The pH of the electrolyte is important for the formation of the porous oxide layers. Especially for Al metals, the porous oxide layer formation disappear and compact oxide formed under neutral and/or alkaline electrolytes [13].

The existence of a self-ordering process is very striking from an electrochemical aspect. The main point affect the growth of porous matrix and there are several factors such as electrolyte (pH), voltage, temperature, and the presence of impurities in the material [14]. When a voltage appeared between anode and cathode, electrode reactions (oxidation and reduction) cause the generation of compact metal oxide layer on the surface of the anode. One of the most important advantages of anodization is simplicity of process. A schematic representation of an anodization cell is shown in Figure 2.2.

The anodized layer on the surface of the metals grows by transferring linear current through an electrolyte by using the metallic sample as the anode (the positive electrode). Hydrogen is carried out at the cathode and oxygen is formed at the surface of the metallic substrate during growth of oxide layer. Anodizing current varies according to area of the metal being anodized and electrolyte content. Electrolyte composition, acidity, solution temperature and current are the main parameters that control the formation of oxide layer.



Figure 2.2 Schematic representation of an anodizing cell.

2.3 Anodic Oxidation of Titanium

In anodization process, current flow from cathode to the anode is possible by using a power source. The anodization can be carried out by applying a constant potential difference between anode and cathode, which is called potentiostatic mode, preferred in this study.

Field-aided transport is dominant for the formation of anodic oxide layer and confirm by the ions in effect to the oxide layer as shown in Figure 2.3. Anodic oxide growth on transition metals materialized long similar process where oxide formation and growth is controlled by field-aided ion transport (O^{2-} and Ti^{4+} ions) through oxide layer. The increase in the oxide layer progress at metal-oxide or at oxide-electrolyte interfaces depending on migration rate of the involved ionic species (Ti^{4+} , O^{2-}).

Firstly, ionization of metal atoms occurs at the anode surface which leads to electron flow from the metal to the cathode due to the existence of external circuit. Ionized metal atoms react with oxygen-containing anions from the electrolyte. As a result oxide solid film grows at the beginning of the anodization process.



Figure 2.3 Schematic diagram of ions diffusing under an electric field (E).

After the formation of the first oxide layer, the growth of this layer continues by the reaction of metal cations and oxygen containing anions. Metal cation formation occurs at the metal/film interface and oxygen containing anions exists at the film/electrolyte interface.

The chemical reactions driven by electrical field during titanium metal anodization process are described as [15]:

At Ti/TiO₂ interface:

$$Ti \to Ti^{2+} + 2e^{-}$$
 (2.1)

At TiO₂/electrolyte interface:

$$2H_2O \to 2O^{2-} + 4H^+ \tag{2.2}$$

$$2H_2O \to O_2 + 4H^+ + 4e^- \tag{2.3}$$

At both interfaces:

$$Ti^{2+} + 20^{2-} \rightarrow TiO_2 + 2e^-$$
 (2.4)

2.4 Experimental Details

Zwilling and his coworkers grew the first self-organized, highly-ordered tubular TiO_2 nanostructures by anodization of titanium and titanium alloy in F⁻ ions containing electrolytes [16, 17]. Grime's group explained the formation of TiO_2 nanotube arrays and the effects of hydrofluoric acid (HF) concentration in electrolyte and applied voltage by using SEM images of oxide layers [18]. A low pH electrolyte was sufficient to create porous oxide layer on the surface of aluminum and its alloys. However, a low pH was not sufficient to solvatize Ti^{4+} and cannot create porous oxide layers were obtained on titanium subjected to anodizing at low pH values [14]. However, the situations become different in the existence of fluoride ions. Some of the key features of fluoride ions are;

- 1. They are able to form water-soluble TiF_6^{2-} complexes. The complex formation aids the prevention of Ti-oxide layer formation at the tube bottom, but this also leads to mild but permanent chemical dissolution of the formed TiO_2 .
- 2. Due to the small ionic radius, fluorides are able to enter the growing TiO_2 lattice and be transported by the applied field through the oxide (competing with O^{2-}) to the metal–oxide interface [19].

Porous titanium oxide growth mechanism which can be seen in Figure 2.4 causes a competition between dissolution and formation of oxide layers that leads to a regular columnar structure growth of TiO_2 film until the steady state condition is achieved.



Figure 2.4 Schematic diagram of oxidation and dissolution reactions of titanium containing metal in the presence of fluoride ion in the electrolyte.

The volume of the oxide that is formed during anodization reaction is larger than the space available to replace the volume of missing metal. This create stress between oxide and base metal and volumetric expansion is the crucial mechanism for the formation of the nanotubular structure. Small fluoride anions can easily diffuse to oxide metal interface by the help of the field distribution which is concentrated at the inner tube bottom as shown in Figure 2.4. Additionally, local acidity changes are observed during typically anodization processes where hydrolyzed cations cause pH drop at the pore tip and enhance chemical dissolution of oxides [20, 21].

At the begining of the process, an oxidized stage forms on the top layer of Ti. If fluoride ion exists on the solution, compact oxide layer decompose and pitting occur by the reaction (1.1).

Self-organized nanotube generation is possible in existence of chemical dissolution. Due to chemical dissolution, the barrier oxide layer thickness decreased and the oxide layer electrochemically etched. This process called field assisted oxidation and dissolution. Nanotubes generation cannot be detected at too high and too low chemical dissolution. The electrochemical etching property hang on anodic oxidation potential and concentration of the electrolyte. If the electrochemical etch proceeds faster than the chemical dissolution, the thickness of the barrier layer increases, which in turn reduces the electrochemical etching process to the rate determined by chemical dissolution [22].



Figure 2.5 Stages during formation of TiO₂ nanotube arrays in fluoride (F⁻) ion containing electrolytes. The detailed transfer of species are shown at the lower right corner.

The nanotube formation begins from small pits generate by local dissolution as shown in Figure 2.5. Especially at the bottom of the pits, both chemical dissolution and electrochemical etching take place. These two reactions decrease the thickness of the barrier oxide layer, which in turn increases the electric-field intensity resulting in further pore growth.

Selective etching take place which means different etching rate of various area on the oxide surface. Different etching rate occurs due to different stress performance on the metal surface [23]. Chemically dissolved ability of the electrolyte removes the top pores and make the unanodized metallic area available for other electrically etching

and dissolution reactions. Separatly formed pore like structure generate formation of nanotubes [22].

Figure 2.6 shows the current transients (I-t curves) recorded during anodizing the samples at constant 20 V in 1 M H_2SO_4 with the addition of different amounts of HF [24]. In pure H_2SO_4 , the typical exponential current decay was observed which can be ascribed to the classical high field oxide formation behavior.



Figure 2.6 Current time transients recorded during anodizing titanium at a constant voltage of 20V. (a) Pure H₂SO₄, (b) with 0.05 wt% HF (c) with 0.15 wt% HF, (d) with 0.3 wt % HF and (e) with 0.4 wt% HF [24].

For electrolytes containing HF, the current episodic digress clearly from H_2SO_4 curve. The current starts rising again with shorter time and at increased HF concentrations. Furthermore, apparent quasi-steady-state value gets higher at higher HF concentrations. Such curves are typical of self-organized pore formation for aluminum and have been dedicated to different stages in the pore formation process [24].

The process consists of;

- i. Current decay leading to the formation of barrier oxide layer
- ii. The current scale up due to formation of random pore and dissolubility of the TiO_2 in fluoride containing solutions
- iii. Cyclic current fluctuation due to outgrowing pores and forming oxide layers competition.

The average amplitude of the periodical current fluctuation increase with increasing HF acid concentration [24]. Numerous studies indicated that the thickness of TiO_2 layer, 1 is almost linearly dependent on the applied potential. As it is given on equation 2.5, voltage, U is inversely proportional to oxide film thickness l. In other words, while field, F is constant, V decreases as l increases.

$$F = \frac{U}{l} \tag{2.5}$$

Since film thickness increases, the solid state migration of ions reduces. This reduction causes the driving force to decrease. The finite thickness reached mainly depends on the anodization voltage. For many transition the final thickness is given by,

$$\boldsymbol{l} = \boldsymbol{f} \boldsymbol{x} \boldsymbol{U} \tag{2.5}$$

where f is the growth factor of the oxide and typically in the range of 2 - 4 nm/V. Typically the layer, which is grown at the oxide/electrolyte interface, consists of lessdense oxide containing oxyhydroxides [19, 25], while the layer at the metal-oxide interface consists of dense and stable TiO₂ [26].

2.5 Controlling the Tube/pore Geometry

In general the pore or tube diameter for Ti metallic substrate reported to be linearly interdependent on the applied anodic potential during growth of metal oxide layer [9, 14, 27]. Nanotube diameters interchange from 10 to 250 nm can be achieved in the

anodization potential 1 to 45 V [9, 28]. However, F^- ion concentration in the electrolyte has no significant effect on the tube and pore geometry of the titanium dioxide nanotube. The major effect of F^- ion occurs in the formation of titanium dioxide nanotubes [22].

According to S. Bauer et al. anodization with constant amount of H_3PO_4 (1 M) with addition of fluoride ion less than 0.1 wt.% results in the generation of a compact oxide layer [25]. At higher fluoride concentrations of 0.1 to 0.4 wt.% self-organized nanotube structures of 50 nm pore diameter was observed. With addition of 0.5 wt.% HF more general etching of the surface was obtained. Titanium dioxide nanotubes formed in H_3PO_4 based electrolyte with the addition of 0.3 wt.% HF concentration at potentials from 1 V to 25 V had self-organized porous structure with diameters changing from 15 to 120 nm and length from 20 nm to 1 μ m [9].

For the H_3PO_4/HF system self-coordinated formation could be achieved even at very low voltages with web-like formation and higher voltages produced larger tube segregation [9]. However, the optimum formation of titanium dioxide nanotubes was possible at 20 V anodizing potential for shorter anodizining times in the same anodic oxidation potential system.

Yasuda et al. [29] found that using Ti and its alloys (TiZr) the nanopore/nanotube diameters associated linear dependency with the buld-up factor of the valve metal oxide. The oxide growth at specific voltage, 20 V, were determined at 0.5 M NH₄F containing electrolyte at various anodizing durations. It was found that the growth rate of TiO₂ nanotube formation decreased to 2.5 nm V⁻¹ until the steady state condition was achieved [30, 31]. Similar results were obtained by Berger et al. [32] using TiAl alloys of different compositions. Above relation was also observed for the formation of titanium dioxide nanotubes from anodization investigations just HF containing aqueous electrolytes [32].

At low anodizing voltage (like 3 V) in electrolytes containing only HF, aggression and tube generation occurs on the surface of the metal. As the voltage increased to 20 V, nanotube structure was formed with an inner diameter of 100 nm, further increase of applied voltage leads to rapid dissolution of titania which results in decrement in oxide thickness and split of the nanotubes [23]. It was observed that highly ordered titanium dioxide nanotube arrays were composed of nanotubes with average inner diameters of 38, 52, and 78 nm corresponding to 10, 15 and 20 V applied potentials respectively [33].

The importance of controlling the tube diameter and length of TiO_2 nanotubes were investigated by Ercan et. al. [34] in terms of biological application with tissue growth parameter. It has been found that the nanotube diameter was one of the most important properties for the antimicrobial behavior. As a result the formation of anodized TiO_2 nanotubes of controlled geometry make the material a strong candidate for the design in future biological applications.

2.6 Electronic Properties of TiO₂

TiO₂ is an n-type semiconductor that has, a band gap energy of 3.2 eV for anatase [35, 36] and 3.0 eV for rutile, [37] or 3.2–3.5 eV in its amorphous state [38]. The relative positions of the band edges vs. some key redox potentials were given in Figure 2.7. Anatase had long electron life time congruently, therefore, TiO₂ has various functional application areas.



Figure 2.7 Electronic structures of different metal oxides and relative positions of their band edges [6].

In 1-D form, the electronic behaviors are very important for various kind application areas, the effect of electricity transportation (way the long path) through oxide to metal material was examined. After the titanium metal is oxidized anodically the formed TiO₂ tubes have an amorphous crystal structure with a band gap of 3.2 eV [21]. Electron and hole pairs can be observed as a result of absorbed photons which have energy of 3.2 eV at least. In order to achieve a current in the external circuit, the electrons have to penetrate through tube boundary to the base metal. An amorphous structure includes lots of defects and/or specific properties. These defects behave as snares and reunification centers for electrical transportation. Previous photo electrochemical studies [21] prove that amorphous TiO₂ tubes have a very low conversion efficiency.

2.7 Applications

Among all transition metals titanium dioxide (TiO_2) is the most comprehensively investigated metal oxide due to its wide application areas including biomedical, electrical, photochemical and environmental. TiO_2 is used in implants, photo catalysts and UV absorbers, sun screens, water hydrolysis and self-cleaning coatings. A list of titanium oxide nanotube application areas and examples is given in Table 2.1.

Table 2.1. Titanium oxide nanotube application areas and ex	amples
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Titanium oxide nanotube application areas					
Biomedical	Photochemical	Electrical	Environmental		
Implants	Antifogging surfaces	Electronic data storage medium	Air purification		
Biomedical coatings	Smart surface coating	Sunscreen	Water treatment		
	Photo catalyst	Dye synthesized solar cells	Self-cleaning coatings		
	UV absorber	Water hydrolysis			

In general, titanium spontaneously forms a stable, protective and strongly adherent oxide layer in air or other oxygen containing environments, because titanium's oxygen affinity is high. The naturally formed oxide layer thickness of titanium is several nanometers (nm) and it is morphologically mainly consisted of homogeneous TiO_2 with amorphous crystalline structures of anatase (tetragonal), rutile (tetragonal) and brookite (orthorhombic). Titanium dioxide (TiO_2) is a main candidate for the nanoscale with large oxidizing power of photo produced holes especially in solar energy objective. In addition, titania is a low cost material relative to its physical and chemical properties.

The proper electrochemical yield of TiO_2 is directly related to high inner surface, better electrically transportation and low charge transfer combination. However, this property can be lost when TiO_2 is in case of solid, liquid or gaseous solution existence. Liquid electrolyte is preferable especially when the structure has a large inner surface area due to nanostructure. Note that contact with electrolyte can be increased by the increment of inner surface area of metal oxide.

In anodization process, well-desired electrochemical solid oxide film grows on a metal substrate. Anodically oxidized TiO_2 nanotubes are self-organized, well-defined and electrically connected to the metal substrates. This type of self-organized anodically oxidized nanotubes has attracted great interest previous 10 years [26]. An anodically oxidized TiO_2 nanostructure represents a particular combination of regular and controllable nanoscale geometry of TiO_2 in terms of tube length, diameter with surface independent substrate. Within this framework, this thesis was devoted to investigate titanium dioxide nanotube formation on Ti6Al4V alloy anodization with various combinations of anodizing duration, electrolyte composition and anodizing voltage.

 TiO_2 nanotubes are linked to metallic material and grows vertically as mentioned in the TiO_2 nanotube formation section. Nanotube structures grow vertically due to electrode charge direction. Nanotubes can be synthesized well-defined top openings and inside volume are regular and controllable [39, 40].

Many of the applications given in Table 2.1 can be attribute to high internal surface areas or shorter diffusion pathways. Catalyst, sensors, ion insertion are example to

several application areas and are frequently based on the use of nanoscaled materials. Many of these applications could be further advanced by a nano scale geometry: such as TiO_2 in photo catalysis [33, 41-43] and for Li ion batteries; [44-46] SnO_2 for sensors; [47] ZnO for photoluminescence [48] and dye-sensitized solar cells [49, 50]. This property is common in almost all transition metals. In addition to this property biologically oxide coated metals are tolerated well by human body [51].

2.8 Photocatalysis (electric) and Dark Photocatalysis

 TiO_2 is the most photo catalytically active material. Fujishima and Honda reported water splitting by light on TiO_2 material in 1972. This resulted in opening a novel approach in heterogeneous kind of catalysis [1]. After this invention, TiO_2 has started to be used as a photocatalyst [2, 3] and this material provides long-term stability. TiO_2 can also be used for the decomposition of undesirable organic compounds with a very low-cost preparation techniques [4–6]. Because it has high activity band-edge position in water environment. The basic principles involved in the photocatalytic mechanism are shown in Figure 2.8. The UV light travels from valence band to conduction band where holes and electrons will be separated. At the end of the separation redox reaction occurs between semiconductor and environment interface.

Alternatively, splitting of water where H^+ and e⁻ can react with H_2O to form H_2 and O_2 can be achieved. At the conduction band, the situation is such that the redox potentials for $O_2 \rightarrow O^{2^-}$ and $H^+ \rightarrow \frac{1}{2} H_2$ are very close. In other words, H_2 generation and O^{2^-} formation are typically competing. At the valence band, O_2 can be formed from water by various pathways, including radicals that can react and finally form O_2 . The reaction rates of the photo catalytic processes on pure TiO₂ are typically limited by the charge-transfer process to a suitable redox species. Therefore, at the valence band, catalysts such as platinum are used to promote.



Figure 2.8. Schematic band diagram of nanostructured TiO₂ and possible photochemical mechanisms when illuminated.

 TiO_2 has very suitable band-edge positions for high photo catalytic activity and the band gap of about 3 eV allows only UV light to be efficiently used. Thus, reactions are commonly performed using suspended nanoparticles or nanoparticulate electrodes. Ordered nanotube arrangements offer various advantages. Moreover, the 1D geometry may allow a fast carrier transport and thus less unwanted recombination losses.

A higher photocatalytic reactivity for TiO_2 nanotubes compared to nanoparticulate layer was reported [52]. Optimized reaction geometry for charge transfer, UV absorption characteristics over the tube and solution diffusion effects were the main effects that makes TiO_2 nanotube high in photocatalytic activity. These findings suggest that in the investigated cases, a valence-band mechanism dominates, and the observed accelerating effects have a common origin in increased band bending, either by junction formation or by the applied voltage [13].

Transition metal oxides detain a wide range of functional properties based on their optical, electrical and chemical behavior including biocompatibility. In their nanostructured form the field of potential applications of these materials is enlarging more. Generally the transition metal oxides can behave as insulators, conductors or semiconductors as outlined in Figure 2.7. Most of them are intrinsic semiconductors
with an n-type behavior (TiO₂, WO₃, ZnO, etc.). However, not only the band gap and the electron kinetics of the material determine the field of application, but also the relative position of the band edges. [53-55]. For this, the conduction band edge needs to lie higher than the species to be reduced (H^+/H_2) and the valence band edge lower than the species to be oxidized (H_2O/O_2). TiO₂, among others, fits these basic requirements comparably well [6].

CHAPTER 3

EXPERIMENTAL METHODS

3.1 Electrochemical Synthesis: Experimental Set-up

The experimental set-up shown in Figure 3.1 was used in this study for titania nanotubes synthesis. The set-up was composed of a two-electrode cell. These cells are connected to a DC power supply. Ti6Al4V (Ti- 6 % Al- 4 % V) samples served as the working electrode (anode) while a stainless steel was used as the counter electrode (cathode). Ti6Al4V sample is placed in the sample holder. The sample is connected to power supply with Ti6Al4V wire which is placed along the sample holder. H₂SO₄ (ACS reagent, 95.0-98.0 %, Sigma-Aldrich) and 0.1 to 0.5 wt.% HF (ACS reagent, 48 %, Sigma Aldrich) containing solutions were used as electrolyte in this study. In first case H₂SO₄ solution was prepared, HF acid amount is arranged accordingly and the total solution water ingredient is balanced.

A cylindrical Pyrex vessel holding the cell was placed into a constant temperature water bath to keep the cell temperature stable during the experiments. Constant and homogenous temperature of the cell was maintained by means a heater employing a magnetic stirrer and a contact thermometer.

Samples served as substrates for anodizing were prepared from extra low impurity (ELI) 18 mm diameter Ti6Al4V titanium alloy rod annealed at 750° C for 1 h. in argon atmosphere. The rod was cut to obtain circular electrodes of 2 mm thickness by using precision cutting machine.



Figure 3.1. The schematic drawing of the experimental set-up used in electrochemical synthesis.

Samples were treated with 600, 800, 1000 1200 grade SiC grinding papers and then polished with 1.3 and 1 μ m diamond paste. Mechanically polished 2 mm thick samples were washed in detergent water mixture to remove oil and degreased by sonicated ethanol, followed by rising with acetone and distilled water to remove dirt and other debris and then dried in air. Samples were eroded by 10 wt. % HF just

before starting each experiment to remove naturally formed oxide layer on the surface of the metals.

The polished samples were mounted to a polypropylene anode assembly to have only the circular surface exposed to electrolyte. During the synthesis, the samples were immersed into the electrolyte while constant cell potentials changing from 10 to 30 V were applied by the DC power supply (Agilent Technologies N8761A System DC Power supply) for the periods of 30 min. to 3 h. The solution considered as electrolyte was varied in composition. Water was used as solvent.

Electrochemical experiments were conducted in 1 M H_2SO_4 with the addition of different concentrations of HF (0.1, 0.3 and 0.5 wt %) solutions. All solutions were prepared from reagent grade chemicals and distilled water after the addition of all chemicals the solution were mixed with a magnetic stirrer to ensure complete homogenization before anodizing step. All anodizing experiments were conducted at room temperature (25°C) with magnetic agitation.

For electrochemical experiments, the samples were placed in the sample holder to confine the surface area to only one side of the sample. Therefore, the area that is going to be oxidized was 10.17 cm². The electrolyte temperature was controlled with a contact thermometer during experiments and the temperature was kept constant at room temperature (25°C). The negative pole of power supply was connected to stainless steel cathode and positive pole was connected to sample (Ti6Al4V) anode. Digital multimeter was connected to set-up to control and record the changes of current during anodization process. After the formation of the porous structures, the samples were immediately and intensively rinsed with distilled water and left in air to dry for subsequent analyses.

3.2 Experimental Design: Minitab

The following study were conducted to validate the effects of the electrolyte composition, anodizing time and applied voltage on titanium dioxide nanotube arrays on Ti6Al4V alloy. The experimental conditions were assessed statistically by using

Minitab [56]. The following factorial design parameters were obtained to develop a relationship between the selected parameters and the results of anodizing tests.

3.2.1 Factorial Design

Studies at least two variables leading to a numerical output are called Factorial Designs. A factor is simply a categorical variable with two or more values. These values are defined as levels. An analyses with 3 factors and 2 levels is named as a 2^3 Factorial Design. In factorial experimental design, a factor is a dominant independent parameter. A level is a subset of a factor.

The use of factorial design brings several advantages including, a greater precision in estimating the overall main factor, interaction between different factors and additional factors. Furthermore, it can help to extend validity of derived conclusions. Factorial designs allow for simultaneous study of several factor effects on a process. Varying the levels of the factors simultaneously rather than one at a time is efficient in terms of time and cost and allows for the study of interactions between factors.

3.2.2 Full Factorial Design

Full factorial design responses are measured at all combinations of the experimental factor levels. The combinations of factor levels represent a condition and each conditions response will be recorded as a response. Each experimental condition is a run and all runs represents an experimental design. By using full factorial design the following data can be obtained;

- 1. Determination of most influential variable.
- Determination of the interaction between/among two or more effects if there is any.

A specific set of experiments were designed to answer above questions. Full factorial design was preferred to conduct all experimental conditions with all variation of the parameters. Table 3.1 shows experimental conditions of a 3^3 three-level, full factorial design with runs in standard order. X, Y and Z were 3 different variables in the experimental set. These three different variables are; anodization potential, anodization duration and HF concentration in electrolyte

for this study. Each experiment was designed with low, medium and high levels of parameters as indicated by 1, 2 and 3 respectively in Table 3.1. For the present study anodization potential levels were 10, 20 and 30 volts, anodization duration levels were 30, 60 and 180 min. and HF concentration levels were 0.1, 0.3 and 0.5 wt. %. There are 27 experimental conditions determined for three parameters of a three-level design.

Experiment	Χ	Y	Ζ
1	1	1	1
2	2	1	1
3	3	1	1
4	1	2	1
5	2	2	1
6	3	2	1
7	1	3	1
8	2	3	1
9	3	3	1
10	1	1	2
11	2	1	2
12	3	1	2
13	1	2	2
14	2	2	2
15	3	2	2
16	1	3	2
17	2	3	2
18	3	3	2
19	1	1	3
20	2	1	3
21	3	1	3
22	1	2	3
23	2	2	3
24	3	2	3
25	1	3	3
26	2	3	3
27	3	3	3

Table 3.1. Full Factorial Design of a 3^3 three-level experimental conditions.

3.3 Characterization: Structure and Composition

The structures and morphologies of the nanotubes, as well as their properties were examined to determine effects of anodizing parameters. X-ray diffraction patterns of the samples were taken by FT (counts) scanning via Rigaku D/Max 2200/PC model X-Ray Diffractometer. Optical microscopic observations were conducted by Olympus PME 3 optical microscope. A series of experiments were performed to examine the morphology of the nanotubes, as well as their properties. For structural and morphological characterization of anodized samples, surface views were taken by FEI Nova NanoSEM 430 scanning electron microscope equipped with energy dispersive X-Ray Spectroscopy (EDS) unit.

3.3.1 Use of ImageJ Program

A series of SEM images were processed and analyzed using ImageJ, an open source image processing program [57] developed by the National Institute of Health, to determine the tube/pore count and diameter under various growth conditions. Typical images of anodized surface are shown in Figure 3.2 to illustrate two alternative nanotube diameter calculations by using ImageJ program.



Figure 3.2. Two alternative titanium dioxide nanotube diameter calculation from the SEM images by using ImageJ program.

The images were converted to an 8-bit image and the black/white threshold values set to yield the inside of each tube/pore as black, while the space in between tubes as white as shown in Figure 3.2. ImageJ automated particle analysis tool was then utilized to count the pores, with each pore being considered as particle. The program outputs were the total particle count, the average size of the particles (in terms of pixels) and their average diameters. To determine the real dimensions, each image pixel length were measured, then the dimensions were determined via a pixel/nm conversion factor. Inner tube diameter direct measurements also carried out in pixels or nm scale and the average values were calculated by the ImageJ program.

3.4 Measurements of Photoelectrical Properties

Only the size and distribution of TiO_2 nanotubes were determined from SEM images and ImageJ program. It is known that the amount of produced power with the photon effect increases as the surface area of TiO_2 increases [58]. Measurements of photoelectrical properties of the samples were conducted to infer comparative information on the surface area which may be used to compare nanotubes. The following experimental set-up shown in Figure 3.3 was used to create photoelectric potentials from anodized samples.

Figure 3.3 shows photoelectrical properties of the nanotube arrays were investigated using a platinum foil as a counter electrode. The samples were placed in a polypropylene sample holder and electrical connections were completed to measure potential differences between two electrodes. The counter electrode was platinum sheet (1 cm x 1 cm). A 1 M KOH solution prepared to be used as the electrolyte solution. Electrical potential of the system was measured by a digital multimeter (Agilent model U1273A) connected to the computer. Measured potential differences recorded on computer for every second of the experiment by using Agilent GUI Data Logger Program.



Figure 3.3. Schematic view of experimental set-up used to measure photoelectrical potentials.

Data measurements were taken dark and illuminated sun light provided by 50 W halogen lamp. Dark curtains were used to darken the sample environment to measure dark current as indicated in Figure 3.3. The measured potential differences were used to drive conclusions on TiO_2 nanotubes.

CHAPTER 4

RESULTS AND DISCUSSION

The X-ray diffraction patterns of the substrate titanium alloy (Ti6Al4V) before and after anodizing are given in Figure 4.1.



Figure 4.1. X-ray diffraction patterns of Ti6Al4V alloy a) before and b) after anodizing process.

Ti6Al4V exhibits two main crystal structures; hexagonal closed packed (HCP, α phase) and body centered cubic (BCC, β phase). The α phase contains %6 aluminum with very low vanadium while β phase contains %4 vanadium. It was observed that diffractions from TiO₂ nanotube film after anodizing could not be identified by X-Ray diffractometer since the thickness of the oxide layer expected to form is very thin.

The results and discussion of the effects of anodizing parameters on titanium dioxide nanotube diameters and their photoelectrical properties are given in this chapter. The numerical values of diameter of TiO₂ nanotube formed at a given anodizing condition are shown in **Error! Reference source not found.** HF concentration applied were; 0.1, 0.3 and 0.5 wt.%. For all experimental conditions electrolyte involved constant amount (1 M) of H₂SO₄. The table includes all TiO₂ nanotube measurements for experimental conditions determined by Minitab experimental design [56]. Three factors; anodization time, voltage and electrolyte concentration were chosen as three levels for the synthesis of the TiO₂ nanotube formation in the full factorial design. The results were obtained by using surface SEM images of the anodized samples. Diameter measurements were calculated from 10 measurements. The effects of the anodization parameters were investigated in detail in the following sections.

HF (wt.%)	Voltage (V)	Time (min.)	Diameter (nm)
0.1	10	30	47 ±3
0.1	20	30	93 ±4
0.1	30	30	158 ± 11
0.1	10	60	48 ±2
0.1	20	60	92 ±6
0.1	30	60	161 ±10
0.1	10	180	44 ±4

Table 4.1. Diameters of TiO₂ nanotubes produced at different anodization conditions.

HF (wt.%)	Voltage (V)	Time (min.)	Diameter (nm)
0.1	20	180	95 ±6
0.1	30	180	165 ±13
0.3	10	30	49 ±3
0.3	20	30	94 ±4
0.3	30	30	166 ±16
0.3	10	60	52 ±3
0.3	20	60	94 ±3
0.3	30	60	124 ±11
0.3	10	180	50 ±4
0.3	20	180	95 ±5
0.3	30	180	138 ±10
0.5	10	30	52 ±4
0.5	20	30	94 ±4
0.5	30	30	144 ±13
0.5	10	60	48 ±5
0.5	20	60	91 ±4
0.5	30	60	150 ±15
0.5	10	180	47 ±3
0.5	20	180	89 ±4
0.5	30	180	146 ±17

Table 4.2. Diameters of TiO_2 nanotubes produced at different anodization conditions (continued).

4.1 Effect of Anodizing Duration

Anodization duration is the uninterrupted time interval during which the process can occur. During the process; time was required for ion migration and diffusion for anodized oxide film formation and growth. The effect of anodizing duration was investigated at constant voltage and constant HF concentrations. To examine anodizing time parameter, the duration was varied from 30 min. to 180 min. for each experimental condition. The SEM results from the surface images of the samples shown in Figure 4.2, were considered to determine the effect of the anodizing duration on titanium dioxide nanotube formation.



Figure 4.2. SEM images of titanium dioxide nanotubes formed in 1 M $H_2SO_4 + 0.5$ wt.% HF at 20 V anodizing potential for a) 30 min. and b) 180min.

Figure 4.2 shows that 30 min. anodizing time was sufficient for the formation of titanium dioxide nanotube layer on the Ti6Al4V alloy at different potentials and

hydrofluoric acid concentrations. However, there were titanium oxide free places on the surface of the metal after 30 min. of anodizing. The oxide formation occurred with dissolution and oxidation reactions on the surface of the metal. For the same anodic potential and electrolyte composition, oxide formation and dissolution rates were different on the surface of the base metal. Titanium dioxide formation on all surfaces took place after 180 min. anodization. SEM studies reveal that titanium dioxide formation can be observed both at 30 and 180 min. anodization time. Uninterrupted time interval was not a dominant factor for the formation of nanotube. However, homogeneities of titanium dioxide nanotube layers were time dependent. SEM image of TiO₂ nanotubes formed in 0.1 wt.% HF electrolyte at 20 V anodizing potential for 60 min. anodizing period was used to investigate lack of formation of TiO₂ nanotubes at certain parts of surfaces as shown in Figure 4.3.



Figure 4.3. SEM image of TiO₂ nanotubes formed in 0.1 wt. % HF at 20 V anodizing potential for 60 min. The lack of nanotubes in dark regions distinguishes the β phase.

As seen in Figure 4.3 dark regions were not covered by oxide nanotubes. The Ti6Al4V samples were composed of hexagonal closed packed α containing higher

Al and higher V containing body centered cubic β phases. Therefore, irregularities in nanotube formation was expected due to different etch attack of the electrolyte for each phase.

Additionally, elemental analyses were conducted by using EDS to investigate the underlying reason of titanium dioxide nanotube free regions. EDS spectra of TiO_2 nanotube free black region in Figure 4.3 is given in Figure 4.4 and weight and atomic percentage of the EDS analysis are given in Table 4.3.



Figure 4.4. The EDS analysis of black region after 30 min. anodically oxidized sample at 20 V in 0.3 wt.% HF concentration electrolyte.

Table 4.3. Weight and atomic percentages of elements based on EDS analyses in Figure 4.4.

Element	Wt. %	At. %
0	6.13	15.81
Al	5.67	8.67
Ti	79.53	68.50
V	8.67	7.02
Total	100	100

According to EDS quantitative and qualitative results, titanium oxide nanotube formation didn't take place during initial 30 min. of the anodization reaction on the alloy containing higher V concentration regions (β -Ti). The lack of oxide formation occurred due to the underlying substrate structure; where vanadium enriched β phase dissolution was faster than α phase.

In Figure 4.5, the EDS analysis of the region where TiO_2 nanotubes were formed after 30 min. anodic oxidation at 20 V in 0.3 wt.% HF concentration electrolyte are given graphically. Weight and atomic percentages of elements taken from the region where TiO_2 nanotubes were formed are given in Table 4.3.



Figure 4.5. The EDS analysis of titanium dioxide nanotube formed region after 30 min. anodically oxidized sample at 20 V in 0.3 wt.% HF concentration electrolyte.

Element	Wt%	At%
0	17.90	37.92
Al	7.37	9.26
Ti	73.86	52.25
V	0.87	0.58
Total	100	100

Table 4.4. Weight and atomic percentages of elements based on EDS analyses in Figure 4.5.

According to results given in Figure 4.5 and Table 4.4, titanium dioxide nanotube formation occurred on the surface of higher Al containing, α phase where oxide formation and metal dissolution rates optimized for the formation of titanium dioxide nanotubes. The result can be explained with reference to the two phase structure of the substrate. Therefore, the dark parts observed in the SEM image, was the result of a different reactivity of α and β phases to the fluoride containing 1 M H₂SO₄ electrolyte.

The SEM images of Ti6Al4V alloy anodized at 10 V in HF acid electrolytes of different concentrations are given in Figure 4.6. The SEM images in each row represent anodization at constant potential with increasing anodization duration from left to right. The images in each column represent anodization for constant duration with increasing HF concentration from top to bottom.



Figure 4.6. SEM images of titanium dioxide nanotube top views formed at 10 V anodic potential a) 0.1 wt.% HF for 30 min. b) 0.1 wt.% HF for 60 min. c) 0.1 wt.% HF for 180 min. d) 0.3 wt.% HF for 30 min. e) 0.3 wt.% HF for 60 min. f) 0.3 wt.% HF for 180 min. g) 0.5 wt.% HF for 30 min. h) 0.5 wt.% HF for 60 min. i) 0.5 wt.% HF for 180 min.

 TiO_2 nanotubes were in general; small, random, connected porous like and selforganized in all cases with similar diameters. Contact diameters and porous like nanotube structures did not change with increasing anodization time from 30 min. to 180 min. in 0.1 to 0.5 wt.% HF containing electrolytes. The variation in inner diameter of nanotubes determined from SEM images by ImageJ program as a function of anodizing duration are shown in Figure 4.7. Although nanotube diameters seem to increase slightly with increasing HF content and decreasing anodization duration, these changes are, in general, smaller than the average uncertainty of 10 nm recorded in this study.



Figure 4.7. Effect of anodizing time on nanotube diameter of Ti6Al4V alloy anodized at 10 V in 1 M H₂SO₄ electrolyte containing 0.1, 0.3 and 0.5 wt.% HF.

The numerical values of inner diameters of TiO_2 nanotubes were between 44-52 nm. As a result, it can be said that inner diameters of TiO_2 nanotubes with both increasing electrolyte concentration and anodization time almost did not change.

The effect of anodization time at 20 V anodizing potential in HF acid electrolytes of different concentrations was determined from SEM images of nanotube structures given in Figure 4.8.



Figure 4.8. SEM images of titanium dioxide nanotube top views formed at 20 V anodic potential a) 0.1 wt.% HF for 30 min b) 0.1 wt.% HF for 60 min c) 0.1 wt.% HF for 180 min d) 0.3 wt.% HF for 30 min e) 0.3 wt.% HF for 60 min f) 0.3 wt.% HF for 180 min g) 0.5 wt.% HF for 30 min h) 0.5 wt.% HF for 60 min i) 0.5 wt.% HF for 180 min.

The SEM images of the TiO_2 nanotube top views in each row represent anodization at 20 V anodic potential with increasing anodization duration from left to right. The images in each column represent anodization for constant duration with increasing HF concentration from top to bottom. From the figure it can be seen that TiO_2 nanotubes were self-organized, tubular like and they were less linked than those observed at 10 V anodizing potential. The diameters of the tubular structures given in Figure 4.9 are larger than those observed at 10 V anodizing potential, but generally not affected from increased anodization time at constant potential of 20 V. The inner diameters of nanotubes produced at 20 V anodizing potential determined from SEM images by ImageJ program as a function of anodizing duration are given in Figure 4.9. Again, small changes in tube diameter with HF content and anodization duration are smaller than the average uncertainty of 10 nm recorded in this study.



Figure 4.9. Effect of anodizing time on nanotube diameter of Ti6Al4V alloy anodized at 20 V anodizing potential in 1 M H₂SO₄ electrolyte containing 0.1, 0.3 and 0.5 wt.% HF.

The numerical values of inner diameters of TiO_2 nanotubes were between 85-96 nm. As a result, it can be said that inner diameters of TiO_2 nanotubes with both increasing electrolyte concentration and anodization time almost did not change.

Investigation of anodization time at 30 V anodizing potential was conducted by using different amount of HF acid in the electrolyte solution. The SEM results of Ti6Al4V alloy anodized at 30 V for different electrolyte composition and anodizing duration

given in Figure 4.10 were used examine the effect anodizing duration at this level of applied potential.



Figure 4.10. SEM images of titanium dioxide nanotube top views at 30 V anodic potential a) 0.1 wt.% HF for 30 min b) 0.1 wt.% HF for 60 min c) 0.1 wt.% HF for 180 min d) 0.3 wt.% HF for 30 min e) 0.3 wt.% HF for 60 min f) 0.3 wt.% HF for 180 min g) 0.5 wt.% HF for 30 min h) 0.5 wt.% HF for 60 min i) 0.5 wt.% HF for 180 min.

The SEM images of the TiO_2 nanotube top views in each row represent anodization at 30 V anodic potential with increasing anodization duration from left to right. The images in each column represent anodization for constant duration with increasing HF concentration from top to bottom. From the figure it can be seen that TiO_2 nanotubes were self-organized, tubular and without interlink between the tubes unlike those seen at 10 V applied potential. The diameters of the tubular structures given in above figure are larger than those observed at 10 and 20 V anodizing potentials, but generally not affected from increased anodization time at constant potential of 30 V.

The inner diameters of nanotubes produced at 30 V anodizing potential determined from SEM images by ImageJ program as a function of anodizing duration are given in Figure 4.11. Nanotube diameters seem to increase slightly with increase in HF content but show very small erratic change with anodization duration. Although these changes are greater than the previous cases the variations may still be considered to be small especially when initial anodization periods are omitted. Furthermore the measured nanotube diameters and their standard deviations were all larger than previous cases.



Figure 4.11. Effect of anodizing time on nanotube diameter of Ti6Al4V alloy anodized at 30 V in 1 M H_2SO_4 electrolyte containing 0.1, 0.3 and 0.5 wt.% HF.

According to Figure 4.11 the numerical values of inner diameters of TiO_2 nanotubes were between 135-165 nm. As a result, it could be said that inner diameters of TiO_2

nanotubes did not change to a considerable extent with electrolyte concentration and anodization duration.

4.2 The Effect of HF Concentration of the Electrolyte

Earlier XPS and SEM analysis of layers anodized at potentials changing from 0 to 5V in electrolytes with and without fluoride ions showed that compact oxide layers of approximately 10 nm thicknesses were formed in both cases. Presence of F⁻ was detected thorough out the layers built in F⁻ containing electrolytes. Therefore, the higher currents observed in current density versus time graph in this initial stage in F⁻ containing electrolytes were related to a fast field-aided F⁻ transport through the growing oxide layer competing with O²⁻ transport. At very short anodization times, the high-field growth of the compact oxide layer was finalized (reaching a steady state thickness) and diffusion effects within the tubes became dominant for the rate control [29] for longer anodization times.

Figure 4.12 shows SEM images of the samples prepared by the 60 minutes anodization treatment at 20 V anodization potential in 0.1 wt.%, 0.3 wt.%, 0.5 wt.% and 1 wt.% HF containing electrolytes.

In all cases shown in Figure 4.12, growth of a nanotube layer was achieved and inner diameters of the nanotubes as was reported in the previous section did not show any significant change in 0.1 wt.%, 0.3 wt.%, 0.5 wt.% and 1 wt.% HF containing electrolytes. Anodization time was just increasing the metal dissolution and titanium dioxide formation. As mentioned previously, fluoride ion existence in electrolyte causes permanent dissolution of anodically oxidized metals. Between nanotube layer and solution, dissolution of metal oxide occurs where oxide formation continues at the metal and oxide interface [59].



Figure 4.12. Surface SEM images of titanium oxide nanotube arryas prepared at 20 V potential for 60 minutes in 1 H_2SO_4 . Addition of a) 0.1 wt% HF b) 0.3 wt % HF c) 0.5 wt % and d) 1 wt % HF were made to electrolyte.

4.3 Effect of Anodization Voltage

In order to explore the potential range for the pore growth, anodization experiments from 10 to 30 V were carried out in the water-sulfuric acid-hydrofluoric acid mixtures. The SEM images of nanopores/nanotubes at above applied potential range were given in previous sections to show effects of HF concentration and anodization duration. The images are repeated here in a different form to illustrate the effect of anodization voltage. A set of SEM images are shown in Figure 4.13 to focus on the effect of applied voltage in 0.1 wt.% HF containing electrolytes. Each row in this figure represents increasing applied voltage from left to right while each column

show TiO_2 structure at constant potential with increasing anodization duration from top to bottom.

From the figure, it can be seen that, other than TiO_2 nanotubes formed at 10 V applied potential, they were tubular and have smooth margins. The increasing trend of TiO_2 nanotube diameters can be seen clearly from the surface images of the samples.



Figure 4.13. SEM images of titanium dioxide nanotube top views formed in 1 M H₂SO₄ + 0.1 wt.% HF electrolyte at a) 10 V for 30 min b) 20 V for 30 min c) 30 V for 30 min d) 10 V for 60 min e) 20 V for 60 min f) 30 V for 60 min g) 10 V for 180 min h) 20 V for 180 min i) 30 V for 180 min.

The inner diameters of nanotubes produced at different anodizing potentials were determined from SEM images by ImageJ program and plotted in Figure 4.14. From the figure, it can be seen that, nanotube diameters increase linearly with increase in applied voltage. High correlation of the linear equations can be seen for different anodizing durations in constant HF containing electrolyte for limited number of data points presented here.



Figure 4.14. Effect of anodization potential on nanotube diameter of Ti6Al4V alloy anodized in 1 M H_2SO_4 electrolyte containing 0.1 wt.% HF for 30 min., 60 min. and 180 min. anodization time.

From previous discussions, it was shown that effects of HF concentration and anodizing duration were not significant within the range covered in this study. Therefore similar SEM images and linear correlations of nanotube diameters are expected at different HF concentrations. Sets of SEM images and corresponding linear correlations showing the effect of applied voltage in 0.3 and 0.5 wt.% HF containing electrolytes are given Appendix I for the sake of completeness.

From above mentioned discussions, it was seen that the key factor controlling the nanotube diameter was the anodization voltage. At low anodic potentials such as 10 V the morphology of the nanotubes had a web like structure rather than a clear tubular morphology. Increasing the potential from 10 V to 30 V increased the inner diameter of the resulting nanotubes. For each experimental set, voltage was a major factor for the determination for the titanium dioxide nanotube diameter regardless of anodizing time and HF concentration.

The nanotube pore size was observed to be proportional to the applied potential. When linear relationships between nanotube inner diameter and anodic oxidation potentials are examined it can be seen that intercept at 0 V is very small. Furthermore, negative nanotube diameter is not expected, but zero diameter at zero potential is logical. Hence they can be related to;

$$d(nm) \sim f \ x \ U \tag{4.1}$$

where, f is the inner diameter growth factor with nanotube diameter (d) and anodic oxidation potential (U). It was therefore found that TiO_2 nanotube diameters increase with increasing anodizing potential by the factor 5.

4.4 Main Effects According to Minitab

The results of the nanotube diameters given in **Error! Reference source not found.** were used to analyze the data to compare correlations discussed above by the results of Minitab program. The equation calculated from the data, excluding the values at 30 V where larger uncertainties were observed, is given as;

$$d(nm) = 0.83 \ HF \ conc. (wt\%) + 5 \ voltage (V)$$
 (4.2)
- 0.01 duration (min.)

From the equation it can be seen that the coefficient of duration (-0.00913) is a very small negative value. It is obvious that the effect of duration is clearly seen to be

insignificant. Although the coefficient of HF concentration (0.83) is larger, but very small HF concentrations (0.1 to 0.5 wt.%) makes this term also small.

The main effect plot is given in Figure 4.15. From the figure, similar to previous conclusions, TiO_2 nanotube diameter can be considered independent of HF concentration in the electrolyte and anodization time. However, the anodization potential was the main factor effecting the TiO_2 nanotube diameters. The constant increasing trend of TiO_2 nanotube diameter with increasing anodizing potential can also be seen in the main effect plot.



Figure 4.15. The main effects plot for TiO₂ nanotube diameter measurements.

4.5 Photoelectric Properties of the TiO₂ Nanotubes

Only the size and distribution of TiO_2 nanotubes were determined from SEM images and ImageJ program. According to Shankar et al., the amount of produced power with the photon effect increases as the surface area of TiO_2 increases [58]. According to SEM results, TiO_2 nanotube diameter was independent of time during anodization within the parameter range covered in this study. Therefore, higher photoelectric potentials should be expected to be produced by samples subjected to longer anodization durations at constant potential. Photoelectric effects of TiO_2 nanotubes formed in 1 M H₂SO₄ + 0.5 wt.% HF electrolyte at 20 V anodic potentials for different anodization durations were tested further to support above expectation. The changes in photoelectric potentials were measured from the cell that produced potentials after providing the light by a 50 W halogen lamp. The measured potentials versus time graphs are given in Figure 4.16.



Figure 4.16. Photoelectric effect of TiO_2 nanotubes formed in 1 M H₂SO₄ + 0.5 wt.% HF electrolyte at 20 V anodic potentials for different anodization durations.

 TiO_2 nanotube diameters were independent of anodization duration and for 20 V 1 M $H_2SO_4 + 0.5$ wt.% HF electrolyte it was about 95 nm for all anodization durations. As it is shown in Figure 4.16 the photoelectrically produced potential increases with increasing anodization duration. Titanium dioxide nanotube surface area on the base

metal expected to be the same since the diameters are equal, therefore, higher potentials can be attributed to longer lengths of the TiO_2 nanotubes.

It was shown that the inner diameters of TiO_2 nanotubes were increasing with increasing applied anodic potential. Photoelectrical properties of the samples formed in 1 M H₂SO₄ + 0.3wt.% HF electrolyte for 180 minutes of anodization at different anodic potentials were tested to deduce comparative information on the surface area, which may be used to compare titanium dioxide nanotubes. The changes in photoelectric potentials produced after providing the light by a 50 W halogen lamp were measured from the cell and shown as potentials versus time graphs in Figure 4.17.



Figure 4.17. Photoelectric effect of TiO2 nanotubes formed in 1 M $H_2SO_4 + 0.3$ wt.% HF electrolyte for 180 minutes anodization duration at different anodic potentials.

According to Figure 4.17, the sample prepared at 20 V anodization potential produced the highest potential difference under illuminated light. Similar potentials were developed from samples formed at 10 V and 30 V applied potentials. The diameters of oxide nanotubes increase with increasing applied anodic potential, therefore surface area and photoelectric potential of the oxide films are expected to become smaller if they have the same length. However, current increases with increasing applied potential. Therefore, there is a competition between the effects of increased diameter and current when applied potential was increased. This competition can be observed in Figure 4.17 where photoelectric effects obtained from samples, which were anodized at 20 and 30 V. From the comparison it can be seen that the growth of nanotubes were not directly proportional to applied potential. The nanotubes formed at 10 V applied potential. Although nanotube diameters were smaller, they were probably not grown much to yield high surface area at 10 V applied potential.

CHAPTER 5

CONCLUSIONS

This research was conducted to investigate the effects of the anodizing potential, duration and HF concentration in 1 M H_2SO_4 solution on the titanium dioxide nanotube diameters and followed by investigating comparative information for the surface areas of the oxide nanotubes by photoelectric measurements. Under optimized electrolyte and oxidation conditions. Controllable TiO₂ nanotubes can be used as a guidance for different oxide nanotube formation procedures and be promising for further investigations to widen application of TiO₂ nanostructures.

According to results:

- Well-ordered titanium dioxide nanotubes are fabricated in aqueous H₂SO₄-HF acid electrolytes at 10 to 30 V anodization potentials over 30 to 180 minutes on Ti6Al4V alloy.
- 2. Anodic oxidation potential was determined as the main factor that effects TiO_2 nanotube diameter. The nanotube diameter is directly proportional to the applied voltage by a factor of 5 nm/V in the voltage range of 10 to 30 V.
- The duration of anodizing and HF acid concentration in the electrolyte did not affect nanotube diameter significantly when the anodic potential is constant. However, homogeneities and the growth of the nanotubes were time dependent.
- The discontinuity of nanotube/nanopore structure is due to the compositional differences of two phase structure of the Ti6Al4V alloy.

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APPENDIX I: Effect of Anodization Voltage



Figure A.1. SEM images of titanium dioxide nanotube top views at constant 1 M H₂SO₄ + 0.3 wt.% HF electrolyte concentration a) 10 V for 30 min b) 20 V for 30 min c) 30 V for 30 min d) 10 V for 60 min e) 20 V for 60 min f) 30 V for 60 min g) 10 V for 180 min h) 20 V for 180 min i) 30 V for 180 min.



Figure A.2. Effect of anodization potential on nanotube diameter of Ti6Al4V alloy anodized in 1 H_2SO_4 electrolyte containing 0.3 wt.% HF for 30 min., 60 min. and 180 min. anodization time.



Figure A.3. SEM images of titanium dioxide nanotube top views at constant 1 M H₂SO₄ + 0.5 wt.% HF electrolyte concentration a) 10 V for 30 min b) 20 V for 30 min c) 30 V for 30 min d) 10 V for 60 min e) 20 V for 60 min f) 30 V for 60 min g) 10 V for 180 min h) 20 V for 180 min i) 30 V for 180 min.



Figure A.4. Effect of anodization potential on nanotube diameter of Ti6Al4V alloy anodized in 1 M H_2SO_4 electrolyte containing 0.5 wt.% HF for 30 min., 60 min. and 180 min. anodization time.