

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL

**INVESTIGATION OF THE GROWTH KINETICS AND MORPHOLOGY
TRANSITIONS DURING POROUS ANODIZATION OF TITANIUM IN
ETHYLENE GLYCOL BASED ELECTROLYTES**



Ph.D. THESIS

Eren SEÇKİN

Department of Materials Science and Engineering

Materials Science and Engineering Programme

MARCH 2022

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**Eren SEÇKİN
(521102004)**

Department of Materials Science and Engineering

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Thesis Advisor: Prof. Dr. Mustafa K. ÜRGEN

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ

**ETİLEN GLİKOL BAZLI ELEKTROLİTLERDE TİTANYUMUN
GÖZENEKLİ ANODİZASYONU SIRASINDA OLUŞAN OKSİDİN BÜYÜME
KİNETİĞİ VE MORFOLOJİK GEÇİŞLERİNİN İNCELENMESİ**

DOKTORA TEZİ

**Eren SEÇKİN
(521102004)**

Malzeme Bilimi ve Mühendisliği Anabilim Dalı

Malzeme Bilimi ve Mühendisliği Programı

Tez Danışmanı: Prof. Dr. Mustafa K. ÜRGEN

MART 2022

Eren SEÇKİN, a Ph.D. student of ITU Graduate School student ID 521102004, successfully defended the thesis entitled “INVESTIGATION OF THE GROWTH KINETICS AND MORPHOLOGY TRANSITIONS DURING POROUS ANODIZATION OF TITANIUM IN ETHYLENE GLYCOL BASED ELECTROLYTES”, which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor : **Prof. Dr. Mustafa K. ÜRGEN**
Istanbul Technical University

Jury Members : **Prof. Dr. M. Kürşat KAZMANLI**
Istanbul Technical University

Prof. Dr. Cengiz KAYA
Yıldız Technical University

Prof. Dr. Servet İbrahim TİMUR
Istanbul Technical University

Asst. Prof. Dr. Fatma BAYATA SOLAK
Bilgi University

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To my father and my mother,



FOREWORD

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February 2022

Eren SEÇKİN
(M.Sc. Metallurgical and Materials Engineer)



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ABBREVIATIONS

AAO	: Anodic Aluminium Oxide
ATO	: Anodic Titanium Oxide
BDT	: Barrier oxide Dissolution Time
COD	: Chemical Oxygen Demand
CSR	: Chemical Shortening Rate
CVD	: Chemical Vapor Deposition
FESEM	: Field Emission Scanning Electron Microscope
FRL	: Fluoride–Rich Layer
PBR	: Pilling–Bedworth Ratio
PVD	: Physical Vapor Deposition
SEM	: Scanning Electron Microscope
UV	: Ultraviolet



SYMBOLS

A	: Frequency factor in Arrhenius equation
BDT	: Barrier oxide layer dissolution time
CSR	: Chemical shortening rate of the nanotubes
E_a	: Activation energy
F	: Faraday constant
GR	: Field-assisted growth rate of the nanotubes
k	: Rate constant
L	: Final length of the nanotubes
M	: Molar mass
Q	: Total charge consumed per cm ²
R_a	: Roughness average
R_q	: RMS (Root mean square) roughness
R_t	: Maximum height of the profile
t	: Anodization duration
T	: Anodization temperature
ρ	: Density



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INVESTIGATION OF THE GROWTH KINETICS AND MORPHOLOGY TRANSITIONS DURING POROUS ANODIZATION OF TITANIUM IN ETHYLENE GLYCOL BASED ELECTROLYTES

SUMMARY

Titanium dioxide (TiO_2 , titania) is a transition metal oxide that has been widely used as a pigment since the early 1900s. The discovery of the photocatalytic properties of the material has made it highly attractive for photovoltaics, photocatalysis, and sensor applications. Besides, titania-based materials have been increasingly employed in the biomaterials industry due to their chemical stability and bio-compatibility. Recently, the production and use of TiO_2 nanomaterials has become popular. The high surface area and possible quantum effects of titania nanostructures have provided significant advantages over micro-size use. TiO_2 nanotubes have attracted great interest among various titania nanostructures, and intensive research has been carried out on their production and use. Although the anodic formation of non-porous barrier oxide films on titanium has been known for decades, the discovery of self-organized nanoporous titania production by anodization in fluoride-containing electrolytes opened a new pathway; and numerous studies have been conducted on the subject.

Preliminary studies on the nanoporous anodization of titanium concentrated on understanding the anodization reactions and controlling the process. Subsequent studies mainly focused on the fabrication of nanotube structures and their use in various applications. Recently, sophisticated studies such as advanced nanotube geometries and doped nanotubes have been prominent. However, the literature shows that the reproducible fabrication of titania nanotubes of desired length and morphology, in a well-ordered structure with a clean surface, is still a challenge. Although many different morphologies have been obtained during anodization, the influence of this morphological variance on nanotube growth has not been defined with a consistent model. One of the main reasons for this deficiency is the insufficient understanding of the anodization process, which reduces effective control over the process. The necessity of a clear understanding of the formation, growth kinetics, and morphological transformations of the nanotubes constituted the main reason for starting this thesis study.

In the first part of experimental studies, investigation and optimization of the anodization parameters (surface condition, stirring, aging of the electrolyte, voltage, temperature, and time) were conducted by utilizing an ethylene glycol-based anodization electrolyte containing 0.6 wt % NH_4F , 1 vol % H_2O . The two-step anodization procedure was optimized to improve the pre-anodization surface. The high surface roughness of the untreated Ti foil could be reduced significantly by the optimized first anodization procedure with an anodization at 50 V and 30 °C for 180 min and subsequent removal of the anodized layer. In the anodization studies carried out under different stirring rates (0 to 1000 rpm), it was observed that the stirring rate has a strong effect on the morphology. The barrier oxide film on the sample surface

disintegrated faster as the stirring rate during anodization increased. It was attributed to the increase in the chemical dissolution rate due to increased agitation. In addition, it was revealed that the increase in stirring rate facilitates effective temperature control.

Experimental studies on the aging and reuse of the anodization electrolyte have shown that current density behavior and morphology can vary significantly depending on the condition of the electrolyte. As the fluoride is consumed by forming water-soluble $[\text{TiF}_6]^{2-}$ species and be solvated during anodization, the amount of free fluorine in the electrolyte gradually decreases. It was experimentally verified that the current density values shift down, and the chemical dissolving power of the electrolyte decreases in anodization conducted after extended usage or short but repetitive usage of the anodization electrolyte. However, it has also been shown that when the electrolyte is kept unused overnight after anodization, almost equivalent current density values and morphological results can be obtained as the anodization performed the previous day. We estimate that when the electrolyte is kept unused for a convenient duration after anodization, $[\text{TiF}_6]^{2-}$ species decompose into TiF_3 , releasing three fluorides (for each molecule); thus, the amount of free fluoride in the electrolyte increases again. In studies examining the effects of anodization voltage and temperature on growth and morphology, it was verified that an increase in either parameter results in an increase in current density and hence an increase in growth rate. In addition, the increase in either parameter affects the morphology by accelerating the chemical dissolution. It was demonstrated that although the voltage has a slight effect on the dissolving power of the electrolyte, the temperature has a strong effect and the chemical dissolution in the electrolyte increases strongly with increasing temperature.

A series of experiments were conducted to observe the effects of the anodization duration on the surface morphology. Three morphologies were obtained in the anodization experiments conducted at 50 V and 30 °C for different durations (5 min to 40 min). For 5 min and 10 min anodized samples, barrier oxide morphology, for 20 min anodized sample open-top nanotube morphology, and 40 min anodized sample nanograss morphology were obtained. It was deduced that the surface morphology during anodization progresses in order of barrier layer, open nanotubes, and nanograss structure, showing that these morphologies are successive processes. Anodization experiments conducted at 50 V and 25 °C for different durations confirmed that the surface morphology changes in the suggested order. It was revealed that there is a correlation between the temperature and the dissolution time of the barrier oxide, which formed the basis of the proposed kinetic model. Additionally, ultrasonication and stripping with scotch tape methods were studied for clearing the sample surface from barrier layer residues and so-formed nanograss.

In the second part of experimental studies, the formation and growth kinetics of the titania nanotubes were investigated by utilizing an ethylene glycol-based anodization electrolyte containing 0.3 wt % NH_4F , 1 vol % H_2O . A model, combining growth with morphology, has been proposed by utilizing the findings obtained in the first part. According to this model, growth is divided into three stages (I. Growth under initial barrier layer, II. Nanopore to nanotube transition, III. Nanograss formation). Stage 1 is defined as the period which includes initial barrier oxide formation, pore initiation, and nanotube growth under gradually dissolving initial barrier oxide. Formation studies conducted at 50 V and 25 °C for different durations (5 sec to 30 sec) demonstrated that ordered nanotubular formation under initial barrier oxide occurs in the early periods of the anodization. We determined that the field-assisted growth of the nanotubes occurs at a constant rate ($\mu\text{m C}^{-1} \text{cm}^2$) at the bottom, under the gradually

dissolving and still protective initial barrier oxide layer. Titanium samples were anodized at 25 °C for different durations (20 min and 80 min) remaining in Stage 1 to determine field-assisted growth rate. In both anodized samples average growth rate of $\sim 0.7 \mu\text{m C}^{-1} \text{cm}^2$ was obtained. It was experimentally observed that the total dissolution time of the initial barrier oxide layer during anodization performed at 25 °C was within the range of 100 – 150 min.

We have defined Stage 2 as the short period after the initial barrier oxide layer is wholly dissolved in which open tube top ordered nanotubes are seen, and nanopore/nanotube transition occurs. As Stage 2 is the sudden transition phase between Stage 1 and Stage 3, it was ignored in the kinetic calculations. Stage 3 is defined as the period for the chemical dissolution of the tube tops and the initiation and progress of nanoglass formation. In this part, the nanotube film's growth and the film's shortening are examined together. Field-assisted growth continues at the bottom with the same efficiency and rate (per coulomb) ($\mu\text{m C}^{-1} \text{cm}^2$) as it is in Stage 1. However, the simultaneous shortening of the tubes due to chemical dissolution occurs at the top at a constant rate (per time) (nm min^{-1}). A kinetic model has been proposed to determine the persistence time of this top barrier layer. According to model, the chemical shortening rate of the nanotubes due to chemical dissolution is determined experimentally by using two different anodization durations remaining in Stage 3, which allows us to calculate the barrier oxide dissolution time (BDT). Barrier oxide dissolution times for 25 °C and 5 °C was calculated as 130.1 min and 414.1 min, respectively, and verified experimentally by anodization conducted for the corresponding BDT values.

The dissolution of the top barrier layer is a chemical process, and its activation energy can be calculated using the experimentally determined parameters that allows us to determine the temperature dependence of BDT. By utilizing 25 °C and 5 °C anodization data and taking BDT^{-1} as the rate constant, the activation energy equivalent to $9.53 \text{ kcal mol}^{-1}$ was obtained for the process. Additional experiments conducted at 35 °C, 15 °C, and -5 °C by using the theoretically calculated BDT values confirmed the model's validity. These calculations and experiments verified that temperature dependence of the barrier oxide dissolution time (BDT) shows Arrhenius-like behavior. Besides controlling the final morphology, it is shown that the plot of nanotube thickness that corresponds to BDT at different temperatures indicates a linear relation; and open-top nanotubes ranging from $6.8 \mu\text{m}$ to $10.4 \mu\text{m}$ can be obtained by tuning anodization temperature and duration according to this model. To summarize, this model gives the opportunity to tailor titania nanotube thickness (within a specific range) and desired nanotube morphology (barrier top, open tube top, or nanoglass) by tuning anodization temperature and duration according to the proposed model.



ETİLEN GLİKOL BAZLI ELEKTROLİTLERDE TİTANYUMUN GÖZENEKLİ ANODİZASYONU SIRASINDA OLUŞAN OKSİDİN BÜYÜME KİNETİĞİ VE MORFOLOJİK GEÇİŞLERİNİN İNCELENMESİ

ÖZET

Titanyum dioksit (TiO_2), 1900'lü yılların başından beri yaygın şekilde pigment olarak kullanılan beyaz renkli bir geçiş metali oksididir. Malzemenin fotokatalitik özelliklerinin keşfi ile, 1970'li yıllardan itibaren fotovoltaiik, fotokataliz ve sensor uygulamalarında kullanılmaya başlamıştır. Ayrıca, titanyum dioksit kaplı yüzeyler ve partiküller kimyasal kararlılıkları ve biyo uyumlulukları ile biyomalzeme endüstrisinde (kemik ve diş implantı) artan şekilde kullanım görmektedir. Son yıllarda titanyum dioksit nanoyapıların üretimi ve uygulaması ön plana çıkmıştır. Nano boyutlu yapıların sağladığı yüksek yüzey alanı ve kuantum etkileri, TiO_2 'nin eşsiz içsel özellikleriyle birleştğinde, uygulamalarda mikro boyutlu kullanıma göre birçok avantaj sağlamaktadır. Çeşitli TiO_2 nanoyapılar arasında nanotüpler büyük oranda ilgi görmüş ve nanotüplerin üretimi ve kullanımı konusunda yoğun araştırmalar yapılmıştır. Titanyum üzerinde kompakt bariyer oksit filmlerinin anodik olarak büyütülmesi uzun yıllardır bilinmektedir. Zwilling ve çalışma arkadaşlarının 1999 yılındaki çalışmasında florür içeren elektrolitlerde gerçekleştirilen titanyum anodizasyonu ile düzenli nano gözenekli titanyum dioksit üretiminin mümkün olduğu raporlamıştır. Bu bulgu yeni bir araştırma alanı oluşturmuş ve florür içeren elektrolitlerde titanyum anodizasyonu üzerine birçok çalışma gerçekleştirilmiştir. Nano gözenekli titanyum anodizasyonu üzerine erken dönemde gerçekleştirilen çalışmalar anodizasyon sürecinin anlaşılması ve kontrol edilmesi üzerinde yoğunlaşmıştır. İlerleyen çalışmalarda, araştırmalar ağırlıklı olarak üretilen titanyum dioksit nanotüplerin çeşitli uygulamalarda kullanımı üzerine odaklanmıştır. Son yıllarda ise, farklı nanotüp geometrileri ve katkılı nanotüpler gibi gelişmiş çalışmalar öne çıkmıştır. Bu çalışmalara rağmen, titanyum dioksit nanotüplerin istenilen uzunluk ve morfolojide, homojen ve düzenli bir yapıda, yüzey kalıntısı olmadan tekrarlanabilir şekilde üretiminin halen bir problem olarak ön planda olduğu görülmektedir. Bunun yanında, anodizasyon sırasında birçok farklı morfoloji elde edilmiş olmasına rağmen, bu morfolojik çeşitliliğin nanotüp büyümesi üzerindeki etkileri tutarlı bir modelle tanımlanamamıştır. Bu problemlerin en önemli nedenlerinden birinin anodizasyon sürecinin yeterince anlaşılması ve dolayısıyla süreç üzerindeki kontrolün yetersiz kalmasıdır. Bu tez çalışması kapsamında titanyum dioksit nanotüplerin oluşum, büyüme kinetiği ve morfolojik dönüşümlerinin anlaşılmasına katkı sağlamak hedeflenmiştir. Bu hedefe yönelik olarak kapsamlı deneysel çalışmalar yürütülerek titanyum metal yüzeyinde oluşan farklı morfolojilerdeki nano yapıların anodizasyon parametreleri ile ilişkisi geliştirilen kinetik modelle açıklanmış ve doğrulanmıştır.

Deneysel çalışmaların ilk bölümünde, anodizasyon parametrelerinin (yüzey durumu, karıştırma, elektrolitin yaşlanması, voltaj, sıcaklık ve süre) araştırılması ve optimizasyonu, ağırlıkça % 0,6 NH_4F ve hacimce % 1 H_2O içeren etilen glükol bazlı anodizasyon elektroliti kullanılarak gerçekleştirilmiştir. İki aşamalı anodizasyon

prosedürü, anodizasyon öncesi numune yüzeyinin iyileştirilmesi amacı ile optimize edilmiştir. İşlem görmemiş titanyum folyonun yüksek yüzey pürüzlülüğünün, 50 V, 30 °C ve 180 dk olarak optimize edilmiş koşullarda gerçekleştirilen bir anodizasyon ve ardından anodik oksit tabanının yüzeyden uzaklaştırılması ile önemli ölçüde azaltılabileceği gösterilmiştir. Farklı karıştırma hızları (0 - 1000 rpm) altında gerçekleştirilen anodizasyon çalışmalarında karıştırma hızının morfoloji üzerinde güçlü bir etkiye sahip olduğu görülmüştür. Anodizasyon sırasında karıştırma hızı arttıkça numune yüzeyindeki bariyer oksit filmi daha hızlı bir şekilde bütünlüğünü kaybetmektedir. Bu durum çözelti içerisindeki artan karışma nedeniyle kimyasal çözünme hızının artmasına bağlanmıştır. Ek olarak, karıştırma hızındaki artışın anodizasyon sırasındaki sıcaklık kontrolünü kolaylaştırdığı tespit edilmiştir. Deneyler sonucunda, anodizasyon deneyleri sırasında 750 rpm karıştırma hızı (2 cm manyetik balık ile) kullanılmasına karar verilmiştir.

Anodizasyon elektrolitinin yaşlanması ve yeniden kullanımı üzerine gerçekleştirilen deneysel çalışmalar, akım yoğunluğunun anodizasyon sırasındaki davranışının ve yüzey morfolojisinin elektrolitin durumuna bağlı olarak önemli ölçüde değişebileceğini göstermiştir. Elektrolit içerisinde bulunan florür iyonları anodizasyon sırasında $[\text{TiF}_6]^{2-}$ iyonlarına dönüşerek çözeltiye geçmekte ve elektrolit içindeki serbest florür miktarı anodizasyon ilerledikçe giderek azalmaktadır. Elektrolitinin uzun süreli veya kısa süreli fakat tekrarlı kullanımından sonra yapılan anodizasyonlarda akım yoğunluk değerlerinin düştüğü ve elektrolitin kimyasal çözme gücünün azaldığı deneysel olarak doğrulanmıştır. Diğer taraftan, bir anodizasyon işlemi ardından elektrolit gece boyunca kullanılmadan tutulduktan sonra gerçekleştirilen anodizasyon işleminde, bir önceki gün yapılan anodizasyon ile hemen hemen eşdeğer akım yoğunluğu değerlerinin ve morfolojik sonuçların elde edilebileceği gösterilmiştir. Elektrolit, anodizasyon sonrası uygun bir süre kullanılmadan bekletildiğinde, elektrolit içerisindeki kararsız $[\text{TiF}_6]^{2-}$ bileşenlerinin TiF_3 'e dönüşerek 3 florür iyonunu serbest bıraktığı (her molekül için) ve dolayısıyla elektrolitteki serbest florür iyonu miktarının yeniden artmasının gözlenen sonuçların nedeni olduğu düşünülmektedir.

Anodizasyon potansiyeli ve sıcaklığının büyüme ve morfoloji üzerindeki etkilerini inceleyen deneysel çalışmalarda, her iki parametrenin de artışının, anodizasyon akım yoğunluğunu arttırarak film büyüme hızını da arttırdığı doğrulanmıştır. Her iki parametredeki artışın da kimyasal çözünmeyi hızlandırarak yüzey morfolojisini etkilediği de saptanmıştır. Anodizasyon potansiyelinin elektrolitin çözme gücü üzerinde zayıf bir etkisi olmasına rağmen, anodizasyon sıcaklığının çok güçlü bir etkiye sahip olduğu ve artan sıcaklıkla elektrolit içerisindeki kimyasal çözünme şiddetini arttığı gösterilmiştir. Bu nedenle, anodizasyon sıcaklığı anodizasyon sonrası oluşan yüzey morfolojilerini de önemli ölçüde etkilemektedir. Anodizasyon süresinin yüzey morfolojisi üzerindeki etkisi de çalışma kapsamında incelenmiştir. 50 V ve 30 °C koşullarında farklı sürelerde (5 dk – 40 dk) gerçekleştirilen anodizasyon işlemleri sonucunda üç farklı yüzey morfolojisi gözlemlenmiştir. 5 dakika ve 10 dakika anodize olan numunelerin yüzeyinde bariyer oksit morfolojisi, 20 dakika anodize olan numune yüzeyinde açık yüzeyli nanotüp morfolojisi ve 40 dakika anodize olan numune yüzeyinde nano çim (nano grass) morfolojisi oluşmuştur. Bu sonuçlar doğrultusunda, anodizasyon sırasında yüzey morfolojisinin bariyer oksit tabakası, açık yüzeyli nano tüpler ve nano çim yapısı sırasıyla ilerlediği ve bu morfolojilerin birbirini takip eden süreçler olduğu sonucuna varılmıştır. 50 V ve 25 °C'de farklı sürelerde gerçekleştirilen anodizasyonlar ile yüzey morfolojisinin bu sıra ile değiştiğini doğrulamıştır. Bariyer

oksitin çözünme süresi ve sıcaklık arasında bir ilişki olduğu belirlenmiş ve bu gözlem tez çalışmasında ortaya konan kinetik modelin temelini oluşturmuştur.

Nanotüplerin yüzeyinde bulunan kalıntıların (bariyer oksit veya nano çim) ultrasonik işlem ve bant yöntemi ile yüzeyden temizlenmesi üzerine çeşitli deneysel çalışmalar da gerçekleştirilmiştir. Literatürde daha önce nano çim için uygulanan bu teknikler, bu çalışma kapsamında bariyer oksit katmanları üzerinde de test edilmiştir. Bu teknikler, zayıf bariyer katmanları ve nano çimin yüzeyden temizlenmesi konusunda etkili gibi görünseler de; pratik olarak uygulanamama, kontrol güçlüğü, tekrarlanabilirlik sorunları ve en önemlisi numune üzerinde bıraktıkları ciddi hasar gibi problemler nedeniyle kullanışlı bulunmamıştır.

Deneysel çalışmaların ikinci bölümünde, titanyum dioksit nanotüplerin oluşum ve büyüme kinetiği çalışmaları ağırlıkça % 0,3 NH₄F ve hacimce % 1 H₂O içeren etilen glikol bazlı anodizasyon elektroliti kullanılarak gerçekleştirilmiş ve ilk bölümde elde edilen bulgulardan yararlanılarak nano yapıların büyüme kinetiği ile morfolojiyi birleştiren bir model ortaya konmuştur. Bu modele göre büyüme süreci 3 aşamaya ayrılmıştır (I. Bariyer oksit tabakası altında büyüme, II. Nanogözeneklerin nanotüplere dönüşümü, III. Nano çim oluşumu). Aşama 1, bariyer oksit katmanının oluşumu, nano gözeneklerin oluşması ve kademeli olarak çözünen bariyer oksit katmanını altında gerçekleşen nano tüp büyümesini içeren süreç olarak tanımlanmıştır. 50 V ve 25 °C'de farklı sürelerde (5 sn - 30 sn) gerçekleştirilen incelemeler, bariyer oksit katmanını altında düzenli nano tüp oluşumun, anodizasyonun erken dönemlerinde meydana geldiği göstermiştir. Nano tüplerin elektrik alan destekli olarak büyümesinin, kademeli olarak çözünen koruyucu bariyer oksit tabakasının altında ve yüke bağlı olarak sabit bir hızda ($\mu\text{m C}^{-1} \text{cm}^2$) gerçekleştiği belirlenmiştir. Nanotüp tabanında gerçekleşen elektrik alan destekli büyüme hızının belirlenmesi için, büyümenin birinci aşaması içerisinde kalacak şekilde, 25 °C sıcaklıkta ve farklı sürelerde (20 dk ve 80 dk) anodizasyon işlemleri gerçekleştirilmiştir. Her iki deneysel parametre için de büyüme hızı $\sim 0,7 \mu\text{m C}^{-1} \text{cm}^2$ olarak bulunmuştur. Ayrıca, 25 °C'de gerçekleştirilen anodizasyonlarda bariyer oksit katmanının tamamen çözünmesi için gereken sürenin 100 - 150 dk aralığında olduğu da deneysel olarak gözlemlenmiştir.

Aşama 2, bariyer oksit katmanının tamamen çözündüğü, yüzeyleri açık nanogözeneklerin görüldüğü ve nanogözenek/nanotüp dönüşümünün gerçekleştiği kısa süreç olarak tanımlanmıştır. Koruyucu tabakanın tamamen çözülmesi ardından, gözeneklerin birleşme noktalarında ve tüp duvarlarının dış kısımlarında yoğun olarak bulunan florürce zengin tabaka öncelikli olarak çözünmeye başlamaktadır. Bu katmanın çözünmesi nanotüplerin net bir şekilde ortaya çıkmasını sağlamaktadır. Büyümenin ikinci aşaması, ilk ve üçüncü aşama arasındaki ani geçiş süreci olduğu için kinetik hesaplamalarda ihmal edilmiştir.

Aşama 3, nanotüplerin üst kısımlarının kimyasal olarak çözünmesi, nano çim oluşumunun başlaması ve ilerlemesini kapsayan süreç olarak tanımlanmıştır. Bu aşamanın anlaşılmasına yönelik olarak nanotüp filminin taban bölgesinde gerçekleşen elektrik alan destekli büyüme ve aynı filmin yüzey tarafında görülen kimyasal çözünme nedeniyle kısılma bir arada incelenmiştir. Büyümenin bu aşamasında da, nanotüp filmi tabanında gelişen elektrik alan destekli büyüme, birinci aşama ile aynı verimle ve yüke bağlı olarak aynı hızda ($\mu\text{m C}^{-1} \text{cm}^2$) gerçekleşmektedir. Fakat bu aşamada, nanotüp filmi yüzeyindeki kimyasal çözünme nedeniyle tüplerin eşzamanlı olarak kısılması da gerçekleşmektedir. Nanotüp filmindeki kısılmanın, elektrolit özelliklerine ve koşullarına göre değişen zamana bağlı sabit bir hızda (nm dk^{-1})

gerçekleştirdiği gösterilmiştir. Bu üst bariyer katmanın kalıcılık süresini belirlemek için bir kinetik model ortaya konmuştur. Nanotüplerin kimyasal çözünme nedeniyle gerçekleşen kimyasal kısılma hızı, büyümenin üçüncü aşamasına denk gelen iki farklı anodizasyon süresi kullanılarak deneysel olarak belirlenebilmektedir. Kimyasal kısılma hızının belirlenmesi bariyer oksit çözünme süresinin hesaplanabilmesini sağlamaktadır. Çalışmada, 25 °C ve 5 °C için bariyer oksit çözünme süreleri sırasıyla 130,1 dakika ve 414,1 dakika olarak hesaplanmış ve hesaplanan sürelerde gerçekleştirilen anodizasyonlar ile deneysel olarak doğrulanmıştır. Modele göre, ağırlıkça % 0,3 NH₄F ve hacimce % 1 H₂O içeren etilen glikol bazlı anodizasyon elektrolitinde, 25 °C’de gerçekleştirilen (50 V, 750 rpm karıştırma) bir anodizasyon sırasında: ilk saniyelerinde nanotüp oluşumu başlamakta ve yaklaşık 130 dakika boyunca ~0,7 µm C⁻¹ cm² hız ile büyümektedir (Aşama 1); sonrasında, nanogözenek/nanotüp dönüşümü meydana gelmekte ve açık yüzeyli nanotüp filmi gözlenmektedir (Aşama 2); 130 dakika sonrasında ise, nanotüp filmi aynı hızla tabanda büyümeye devam ederken (~0,7 µm C⁻¹ cm²) eşzamanlı olarak anodizasyon sonuna kadar ~19,4 nm dk⁻¹ hızla kısılmaktadır (Aşama 3).

Üst bariyer oksit katmanının çözünmesi kimyasal bir süreç olduğu için, çözünme süresinin sıcaklığa bağlı değişimi gösteren aktivasyon enerjisi deneysel olarak elde edilen veriler ile hesaplanabilir. 25 °C ve 5 °C anodizasyon verileri kullanılarak ve bariyer oksit çözünme süresinin tersi (BDT⁻¹) hız sabiti olarak alınarak, bariyer oksit çözünme süreci için 9,53 kcal mol⁻¹ aktivasyon enerjisi değeri elde edilmiştir. 35 °C, 15 °C ve -5 °C için bariyer oksit çözünme süreleri teorik olarak hesaplanmış ve bu sürelerde gerçekleştirilen anodizasyon deneyleri ile modelin geçerliliğini doğrulamıştır. Bu hesaplamaların ve deneylerin sonuçları, bariyer oksit çözünme süresinin sıcaklığa bağlı değişiminin Arrhenius denkleminin uyan bir davranış gösterdiğini doğrulamıştır. Ayrıca, farklı sıcaklıklardaki bariyer katman çözünme süreleri parametre olarak kullanılan deneyler sonucunda nano tüp film kalınlığı ile anodizasyon sıcaklığı arasında doğrusal ilişki olduğu da göstermiştir. Bu doğrusal bağıntı, yapılan ek deneyler ile doğrulanmış ve yüzeyleri açık nano tüplü yapılar elde edilmiştir. Tez çalışması sonucunda ortaya konulan özgün model ile anodizasyon sıcaklığı ve süresi ayarlanarak istenen kalınlıkta ve istenen morfolojide (bariyer, açık nanotüpler veya nanoçim) titanyum dioksit nanotüp filmlerinin üretilebileceği gösterilmiştir.

1. INTRODUCTION

Titanium dioxide (TiO_2 , titania) is a white, water-insoluble transition metal oxide that has been widely used as a pigment since the early 1900s [1]. With the understanding of the semiconducting and photocatalytic properties of the compound, it has started to be utilized in many different applications such as photovoltaics, photocatalysis, and sensors in the last 50 years [2–6]. Besides, with its biocompatibility and high chemical stability, TiO_2 has also gained significant interest in the biomaterials sector, and intensive studies have been conducted on the topic [7]. Structurally, titania has three different polymorphs with different formation temperature ranges (anatase, rutile, and brookite). Among these, anatase and rutile forms are the most utilized forms of TiO_2 in many applications with their chemically stable structure and high photoactivity. [8,9].

In recent years, the production and application of titania nanostructures (nanoparticles, nanotubes, nanowires, nanorods, nanosheets) have become prominent. The high surface area and quantum effects provided by the nanoscale structures, combined with the outstanding intrinsic properties of TiO_2 , have opened up potential use in many different applications [10,11]. Among various TiO_2 nanostructures, nanotubes have received significant attention, and intensive research has been conducted on their use in solar cells, photocatalysis, sensors, and biomaterials applications [12–14]. Even though the fabrication of barrier oxide films on titanium by anodization has been known for many years, Zwilling et al.'s work in 1999 showed for the first time that self-organized titania nanotubes could be produced by anodization in electrolytes containing fluoride ions [15–17]. TiO_2 nanotubes have been produced by four different methods (hydrothermal, template, electrospinning, and anodization). The most straightforward, relatively fast, and low-temperature process among them is the anodization method, which is extensively used to produce titania nanotubes [9,12].

Nanoporous anodization of titanium is based on anodic charging of titanium in a fluoride-containing electrolyte against a suitable cathode. Performing the anodization in fluoride-containing electrolytes enables the transformation of the formed oxide into

water-soluble fluoridated titanium species ($[\text{TiF}_6]^{2-}$). Selective dissolution of this species allows the formation of self-ordered nanotubular structures under optimized anodization conditions [18]. With the initiation of anodization, a barrier oxide layer is formed, similar to the anodization in fluoride-free electrolytes. However, in the case of anodization in fluoride-containing electrolytes, random pit formation occurs immediately on the surface due to the interaction of fluoride ions with the oxide. These pits act as low resistance regions and cause the electric current to flow through these regions. As the anodization progresses, these pits deepen to form pores and, subsequently, nanotubes. The mechanism that allows nanotubes to grow into the sample is field-assisted formation and dissolution at the tube base (due to fluoride ions). On the other hand, chemical dissolution occurring on the other parts other than the tube base (especially on the tube surface) negatively affects the nanotube growth. The growth process of nanotubes is tuned by balancing these two effects [12].

Titania nanotubes grown by anodization can be grouped under 3 generations depending on the electrolyte composition and properties. First-generation nanotubes have been grown in HF containing aqueous electrolytes (acidic, non-viscous); second generation nanotubes have been grown in aqueous solutions of fluoride salts (NH_4F , NaF) (neutral, non-viscous); and third-generation nanotubes have been grown in neutral organic solutions (i.e., glycerol or ethylene glycol) of fluoride salts (NH_4F , NaF) (neutral, viscous). While the final nanotube lengths produced in the first and second-generation electrolytes are limited to a few microns, it is possible to produce hundreds of microns long TiO_2 nanotubes in the third-generation electrolytes. In today's studies, third-generation electrolytes are frequently used, and nanotubes in various sizes, shapes, and morphologies are investigated for use in many different applications [19].

Early studies of nanoporous titanium anodization focused on understanding and controlling the anodization process. In the subsequent studies, researchers focused more on the use of fabricated titania nanotube structures in various applications, and the number of new studies on formation and growth has relatively decreased. More sophisticated studies such as advanced nanotube geometries and doped nanotubes have become prominent in recent studies. Despite these intensive studies, TiO_2 nanotubes have not found significant use in commercial applications, unlike the widespread commercial use of aluminum oxide nanotubes. Considering that anodic porous

alumina films were first reported in 1953 and intensive studies have been carried out over the years, the porous anodization of titanium appears to be a relatively young technology [20]. When the studies in the literature are examined, it is seen that the reproducible production of titania nanotubes in the desired length and morphology, in a homogeneous and regular structure, without surface residues is still a challenge. One of the primary reasons for this difficulty is the insufficient understanding of the anodization process and thus the lack of intelligent control over the process. The necessity of a clear understanding of the formation, growth kinetics, and morphological transformations constituted the main reason for starting this thesis study, which aims to contribute to the understanding of the titanium anodization processes.

Many different parameters affect the anodization process and nanotube growth. Among these parameters, the major anodization parameters such as anodization electrolyte composition, anodization voltage, temperature, and duration have been studied extensively, and their effects on nanotube growth have been determined. In general, the anodization electrolyte affects the growth process and the final nanotube length in different ways depending on the pH and the viscosity [21,22]; higher anodization potential results in larger tube diameter and higher growth rate [23]; increase in anodization time results in thicker films (especially in organic electrolytes) [24]; higher anodization temperature increases ion migration, thus growth rate of the oxide film, and has a mild effect on tube diameter [25]. The other parameters (minor parameters) such as sample surface condition, stirring effect, re-usage of the anodization electrolyte, cathode material and size, anode-cathode distance have been less studied in terms of their effects on titanium anodization. Although the effect of anodization parameters on nanotube growth is reasonably well defined, there is no complete consensus regarding their effect on the final morphologies of the nanotubes.

Current time behavior under constant anodization voltage can be used to follow porous titania films' growth stages. At stage I, a barrier oxide layer is formed immediately before pore initiation, causing a sharp decrease in current density [26]. At stage II, fluoride ions in the electrolyte stimulate the pitting in the barrier oxide layer (pore initiation), and an increase in the anodization current is observed as the resistance of the anodic film decreases [27]. At stage III, nanotubes start to grow from initiated pores, and the current goes into a gradual decline period as the nanotubular oxide film

grows thicker [28]. Porous film thickness increases with time as more current passes through the system. A disordered top layer (nanograss), which is not favored in many applications because of its irregular and loose structure, may form under extended anodization duration [29]. Some studies have shown that, by protecting the top barrier oxide layer, longer tubes without nanograss could be obtained, attributed to restricted chemical dissolution of the grown nanotubes by preventing contact with the electrolyte [29–34]. On the other hand, in several other studies, nanograss structure was removed by ultrasonication [35] or stripping with scotch tape [36], which has the potential of severely damaging nanotube films.

The growth kinetics of nanotubes have been studied using different approaches. The dependence of nanotube growth rate on temperature, voltage, and time was investigated under potentiostatic [37–41] and galvanostatic conditions [42,43]. Additionally, the effects of the bottom barrier oxide layer on growth [44,45], pore initiation [46], and anodization reaction kinetics [47] have been studied. As will be explained in detail in the following sections, in the kinetic studies, efforts were made to formulate the effects of anodization parameters on growth and determine the optimum growth conditions. Several studies suggested that nanotube growth is thermally activated and obeys the Arrhenius equation. Mathematic models were proposed to estimate the final length of the nanotubes depending on the anodization parameters, and the models were tested with literature data. Even though some models showed consistency with some data sets, they showed inconsistency with others and gave a very high error ratio in several data sets.

Although essential findings have been obtained in the studies, a kinetic model approach still lacks combining the growth process with the final morphologies of the different nanotubular structures. Although nanotube growth under the initial barrier layer was suggested in an early work [28] and mentioned in several studies [9,48], it has not been considered in most kinetic studies. On the other hand, it has been well observed that extended anodization durations cause irregular nanograss structures. However, attempts have been mainly focused on suppressing the nanograss formation [29–34] or removing the so-formed nanograss structure [35,36] instead of investigating the formation kinetics and controlling the process. In several works, the initial barrier oxide layer, open tube top nanotubes, and nanograss structures were shown in the same study. However, they were interpreted as morphologies caused by different

anodization conditions instead of different stages of the growth process [24,49]. Moreover, the influence of this morphological variance on nanotube growth has not been defined with a consistent model. In most of the kinetic studies, the final length of the nanotubes has been used as the main parameter for defining kinetics of the growth process [37–39,41], and different characteristics of growth stages have not been considered. Therefore, kinetic models for nanotube growth have not provided consistent results that always satisfy the experimental findings.

In the first part of experimental studies, parameters affecting the anodization process were investigated and optimized to understand the nanotube growth process better and determine reproducible conditions for kinetic studies. One of the critical problems observed in the literature is that most of the kinetic studies were carried out under atmospheric conditions, which causes the growth behavior to change during anodization because of the water absorption of the electrolyte. In this study, all procedures were conducted inside a glovebox so that the strong hydrophilic character of ethylene glycol-based electrolytes does not affect the anodization process. A frequently used electrolyte composition was chosen and employed to investigate the anodization parameters. Primarily, minor parameters (listed above) were investigated and optimized to ensure the reproducibility of the experiments. In two-step anodization studies, an optimum condition was determined by examining the effects of the first anodization duration on the roughness of the surface. The effect of the stirring rate on the growth and stabilization of the electrolyte temperature was investigated. In electrolyte aging and re-utilization studies, the effect of repeated use on the anodization electrolyte was investigated. An unusual behavior of the electrolyte that strongly affects anodization current density was observed and interpreted. As a result, optimum conditions were determined to be used in kinetic studies to ensure reproducible results. Secondly in this part, the effect of major parameters (voltage, temperature, and time) on the nanotube formation and morphology transitions were investigated. As a result, a unique link between major anodization parameters and morphology transitions was observed, revealing that different morphologies are strongly associated with the dissolution of the initial barrier oxide layer. Detailed investigations of this finding were carried out in growth kinetics studies.

In the second part of experimental studies, the formation and growth kinetics of the TiO₂ nanotubes were investigated. In order to observe and evaluate the morphological

transformations during the formation and growth of nanotubes, time-dependent systematic experiments were carried out at different temperatures. This section propose a new model approach for determining the formation and growth kinetics of different titania structures during anodization in ethylene glycol-based electrolytes. According to this model, we divided the growth process into three stages (I. Growth under initial barrier layer, II. Nanopore to nanotube transition, III. Nanograss formation) and evaluated the stage-dependent nanotube growth kinetics. As will be explained and verified later, the reason for this division is the inability to apply the same growth mechanism to different stages of growth. At the first stage, the nanotube growth kinetics under chemically and gradually dissolving protective barrier oxide is investigated, employing a total charge passed through the system during anodization. At the second stage, after accomplishing the chemical dissolution of the top barrier layer, a well-defined nanoporous structure appears. This structure is unstable and converts into nanotubes in a short period. At the third stage, nanograss formation starts on the top of the nanotubes. To determine the growth kinetics of nanotubes and conversion of them into nanograss, the simultaneous influence of field-assisted nanotube growth and chemical dissolution of the tube tops (shortening of the tubes) are taken into account. Morphology transitions during anodization and growth kinetics at the proposed stages were experimentally investigated and verified to be compatible with the suggested model. This model approach was produced based on determining chemical dissolution kinetics of the initial barrier oxide layer formed on the nanotubes, which is a temperature-dependent process and found to fit well with the Arrhenius equation. By using this approach, it has been shown that morphology (barrier top, open tube top, or nanograss) and thickness of the nanotubes can be estimated under modeled conditions; and desired morphology and nanotube thickness can be obtained by tuning anodization temperature and duration.

2. LITERATURE REVIEW

2.1 TiO₂ and Nanostructured TiO₂

Titanium dioxide (TiO₂, titania) is a transition metal oxide extensively used in various industries with its distinctive features. Since the early 1900s, titania has been widely used as a white paint pigment in many industries, including the food industry, because of its pure white color and non-toxic nature [1]. In 1972, the photocatalytic water splitting feature of TiO₂ under UV light was discovered; and this paved the way for many studies on different applications of TiO₂ [2]. The electronic structure of titania (wide band gap n-type semiconductor) has allowed it to be used in various photovoltaics, photocatalysis, and sensor applications [3]. TiO₂ has been used in photovoltaics as a matrix for electron donor materials and as the charge carrier in dye-sensitized and perovskite solar cells [4]. Furthermore, titania structures have been extensively employed as catalysts in many photocatalysis applications such as water splitting, carbon dioxide conversion, pollutant degradation [5]. Moreover, TiO₂-based materials have been widely studied to be utilized in various sensor applications such as gas sensors, COD (chemical oxygen demand) sensors, and biosensors [6]. On the other hand, titania-coated surfaces or powders have been increasingly employed in the biomaterials (bone and dental implants) industry because of their chemical stability and bio-compatibility. Besides, surface-modified TiO₂ structures have been used in stent applications and for drug delivery [7].

TiO₂ has three crystalline forms (anatase, rutile, and brookite). Anatase and rutile are the photoactive forms of titania with band gap values of 3.2 eV and 3.0 eV, respectively. [8]. Pure anatase or anatase/rutile mixture is employed in most TiO₂ applications. Titania nanostructures produced under low-temperature conditions are generally in amorphous form. Heat treatment is applied to the structure to transform the amorphous phase to anatase (~ 300-500 °C) or anatase/rutile mixture (~ 500-700 °C). Phase transition temperatures can shift within a range depending on the material's structural properties such as particle size, strain, surface roughness, impurities, etc. [9].

TiO₂ nanostructured materials have gained significant interest in recent decades, and intensive academic studies have been conducted on the structures' production, properties, and potential uses. Titania nanostructured materials with different morphologies such as nanoparticles, nanotubes, nanowires, nanorods, nanosheets have been developed and employed in various applications to utilize the geometry and structure specific advantages [10]. The major advantage of the nanomaterials is the very high surface area per unit volume of the structure. The smaller size of the nanostructures ensures that the surface area where the reaction/interaction occurs increases significantly, resulting in an enhanced reaction rate or stronger interaction [11]. As the size of nanostructures decreases, the surface area/volume ratio increases drastically. Besides, by decreasing size to the nanometer scale, new physical and chemical properties caused by quantum effects start to emerge, such as quantum confinement, which significantly affects electron and hole transport in semiconductor nanomaterials [10]. TiO₂ nanostructured materials are produced using many different approaches, including sol method, sol-gel method, micelle method, hydrothermal method, solvothermal method, anodic oxidation, CVD, PVD, electrodeposition, sonochemical method, and microwave method [10].

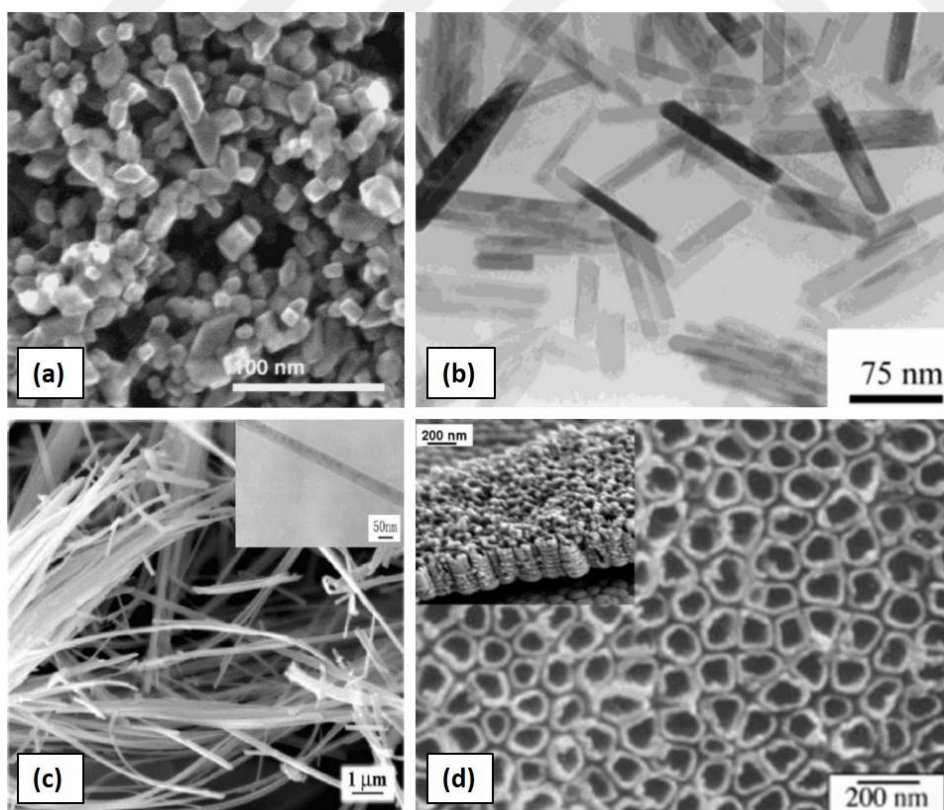


Figure 2.1 : Examples of different TiO₂ nanostructures [10]: (a) Nanoparticles, (b) Nanorods, (c) Nanowires, (d) Nanotubes.

2.2 TiO₂ Nanotubes

Titanium dioxide nanoporous structures have gained significant interest due to their unique properties (ordered morphology, high surface area, wide-bandgap, chemical inertness, biocompatibility, etc.), making them the material of choice in various applications, including biomaterials, solar cells, photocatalysis and sensors [12–14]. Although the anodic formation of non-porous barrier oxide films on titanium has been known for decades [15,16], the revolutionary study of Zwillig et al. in 1999 reported the possibility of production of self-organized nanoporous titania by anodization in fluoride-containing electrolytes. This finding opened a new pathway; numerous studies have been conducted on titanium anodization in fluoride-containing electrolytes [17].

TiO₂ nanotubes have been successfully synthesized by four different methods: hydrothermal, template, electrospinning, and anodization [9]. Hydrothermal synthesis of titania nanotubes is realized by treating titania powders in an alkaline medium (NaOH) at high temperatures (100 to 180 °C) for several days. As the result of the process, thin-walled and open-ended individual titania nanotubes are formed separately or in bundle structure [50]. It is not possible to obtain ordered nanotube arrays in the hydrothermal method, and it is also a time-consuming method as the processing time is on the scale of days. In the template method, titania nanotubes are formed by filling the pre-prepared template by electrophoresis or sol-gel and subsequent selective dissolution of the template. Templates are frequently made of AAO (anodic aluminum oxide) or ZnO (zinc oxide) [51,52]. Although it is possible to produce a well-organized nanotubular structure using the template method, it is impractical as it involves many production steps. TiO₂ nanotube production by electrospinning method is based on coating pre-prepared polymeric fibers with titania and then burning off the fiber by a thermal treatment. Like the hydrothermal method, this method also leads to forming individual nanotubes separately or in a bundle form [53]. It is not a practical method as it contains many steps, including producing the fibers, coating, and thermal treatment. Anodization of titanium is the most straightforward one-step process to produce TiO₂ nanotubes. In this method, titanium is anodically polarized in a fluoride-containing electrolyte. Oxidation and selective dissolution of titanium oxide coincide, allowing the formation of self-ordered nanotube arrays under optimized conditions [12]. As it is a relatively short and low-

temperature process, anodization has been a highly accepted process for producing titania nanotubes.

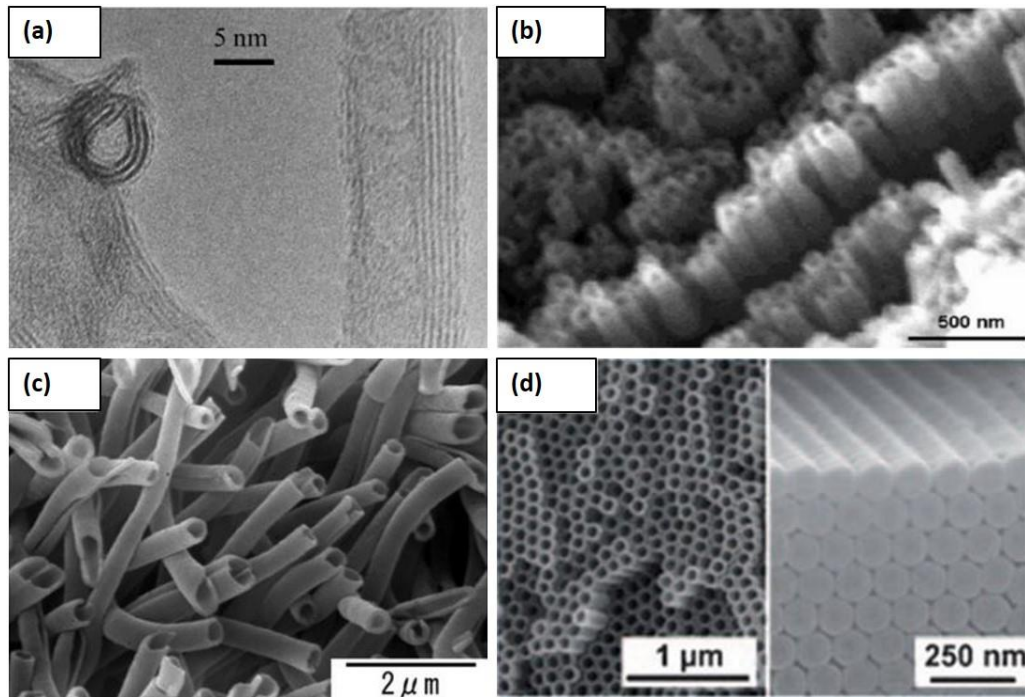


Figure 2.2 : Typical TiO₂ nanotube morphology produced by different methods [9]: (a) Hydrothermal, (b) Template, (c) Electrospinning, (d) Anodization.

Individual nanotubes (as it is formed in hydrothermal and electrospinning methods) show similar characteristics to nanostructures such as nanoparticles, nanowires, and nanorods and can be used as a functional additive or a disordered matrix. On the other hand, ordered nanotubes (produced by anodization) directly attached to a surface have some distinct advantages besides high surface area. For instance, in solar cell and photocatalysis applications, ordered nanotube arrays reduce the recombination losses and allow electrons to be transmitted fast and efficiently by their continuous and dense structure [24,54]. Additionally, anodization leads to the direct growth of nanotubes on the titanium surface, resulting in a firm attachment to the base; and this allows the possibility of using titania nanotubes in biomedical implant applications where strong adhesion is essential [55].

2.3 Titanium Anodization

Porous anodization of titanium is conducted by polarizing titanium anodically across a suitable cathode material (platinum, stainless steel) in a two-electrode electrochemical cell containing fluoride ions. A compact oxide layer is formed by

anodization in an electrolyte that does not contain fluoride ions, and a nanotubular TiO₂ layer is formed as a result of anodization in an electrolyte containing fluoride ions (Figure 2.3). The presence of fluoride in the electrolyte leads to oxidation of the metal and selective dissolution of the formed oxide simultaneously. Self-organized regular pore structures are obtained under optimized conditions [18].

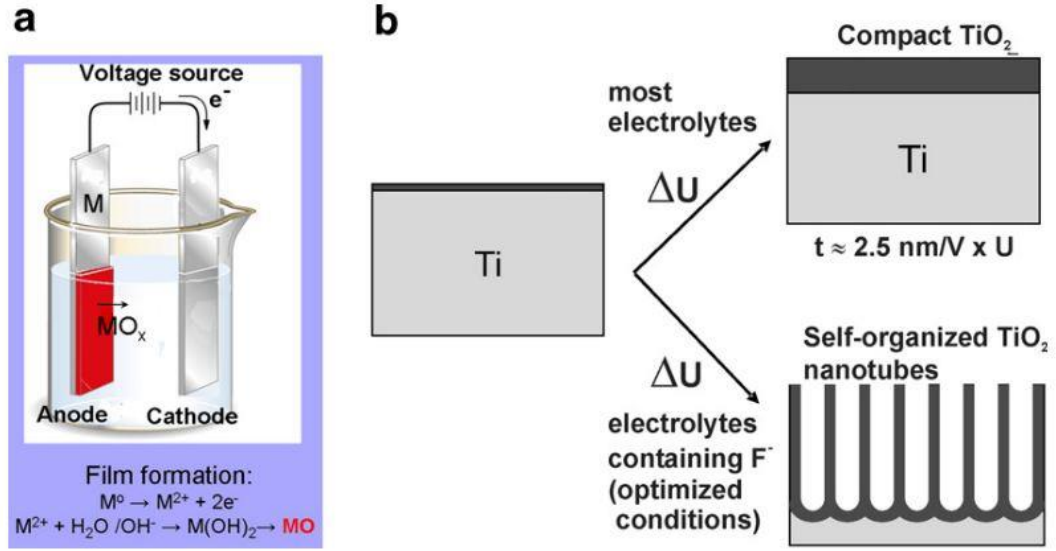
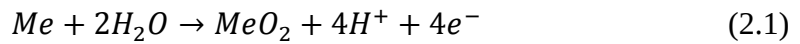


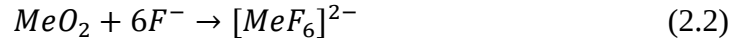
Figure 2.3 : Schematic representation of the Ti anodization process [18]: (a) Typical anodization setup, (b) Anodized TiO₂ morphology in absence/presence of fluoride.

Compact oxide formation is occurs according to the equation 2.1:



Oxide growth is controlled by the transport of ions (Ti⁴⁺ and O²⁻) through the oxide layer with the electric field's contribution produced by the applied potential. If the system is under constant electric potential, the electric field along with the oxide gradually decreases as the oxide film thickens and drops to zero at a certain point. The final thickness of the compact oxide is directly related to the applied voltage and generally in a range of 1-3 nm.V⁻¹ depending on the anodization condition. The current density passing through the system is at its highest level at the start of the process and decreases logarithmically to zero as the oxide reaches the limit thickness [13,16].

On the other end, when it comes to titanium anodization in a fluoride-containing electrolyte, fluoride ions involve in the selective dissolution of the oxide. Fluoride ions interact with compact TiO₂ on the oxide-electrolyte interface and form water-soluble [TiF₆]²⁻ complexes according to equation 2.2:



In addition, Ti^{+4} ions that reach the oxide-electrolyte interface due to the electric field through the oxide are solvated concurrently by fluoride ions, according to equation 2.3:

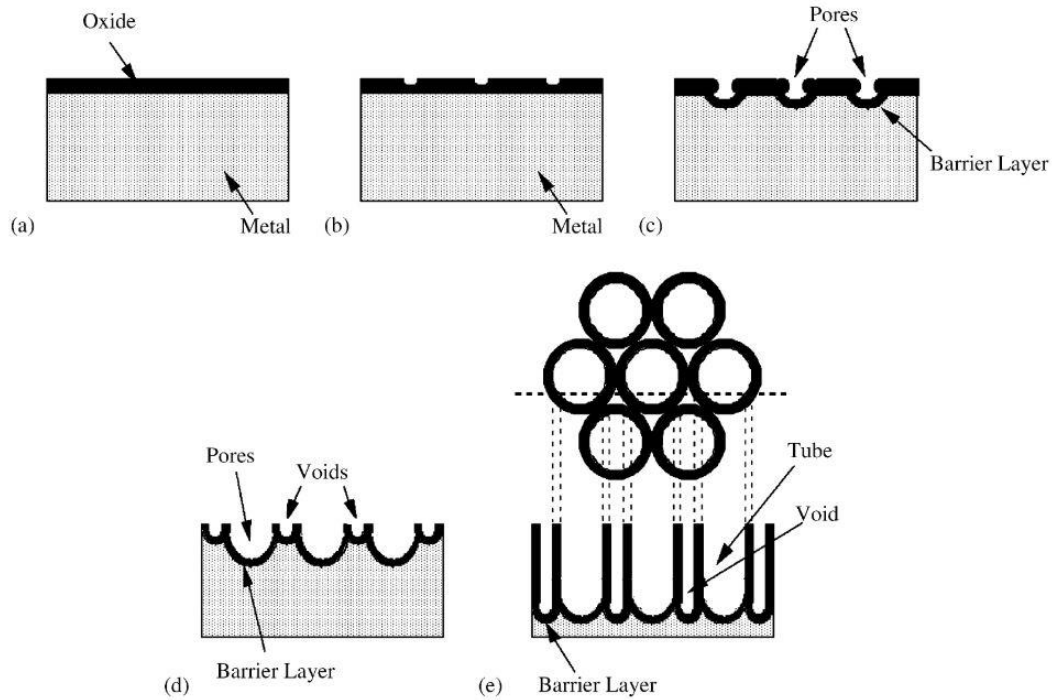
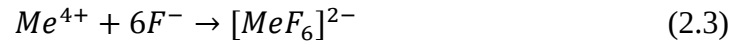


Figure 2.4 : Schematic representation of the TiO_2 nanotube formation [12]: (a) Compact oxide formation, (b) Random pit formation, (c) Transition of pits to the pores, (d) Chemical dissolution between the pores, (e) Nanotube array.

At the beginning of anodization, the initial barrier oxide layer forms on the surface rapidly (Figure 2.4(a)). Then, random cavities form on the surface by the complex-forming effect of fluoride ions in the electrolyte (Figure 2.4(b)). These cavities provide short-term electric resistance drop and allow electric current to flow selectively through them (Figure 2.4(c)). In this way, cavities deepen to form nanotube due to the field-assisted oxidation and dissolution reactions that occur at the bottom of these cavities (Figure 2.4(d)). In optimized conditions, where the current density is evenly distributed over the sample surface, formation of highly ordered nanotube films become possible (Figure 2.4(e)) [12].

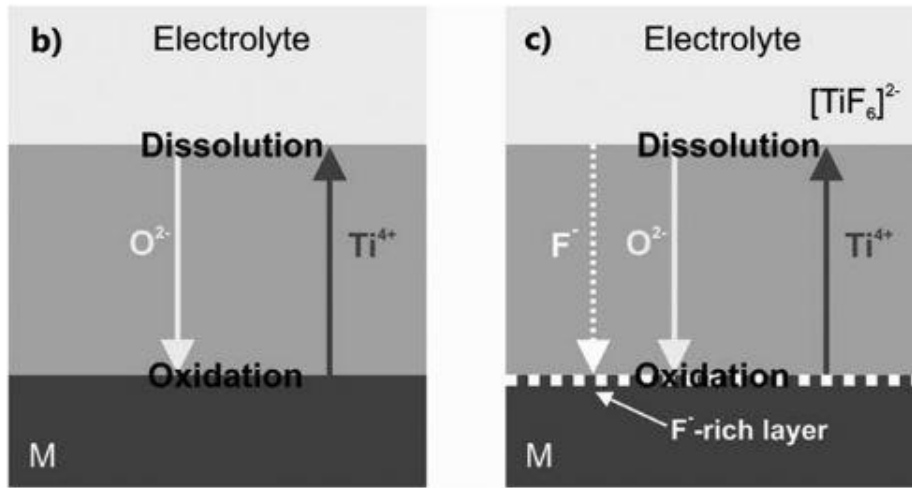
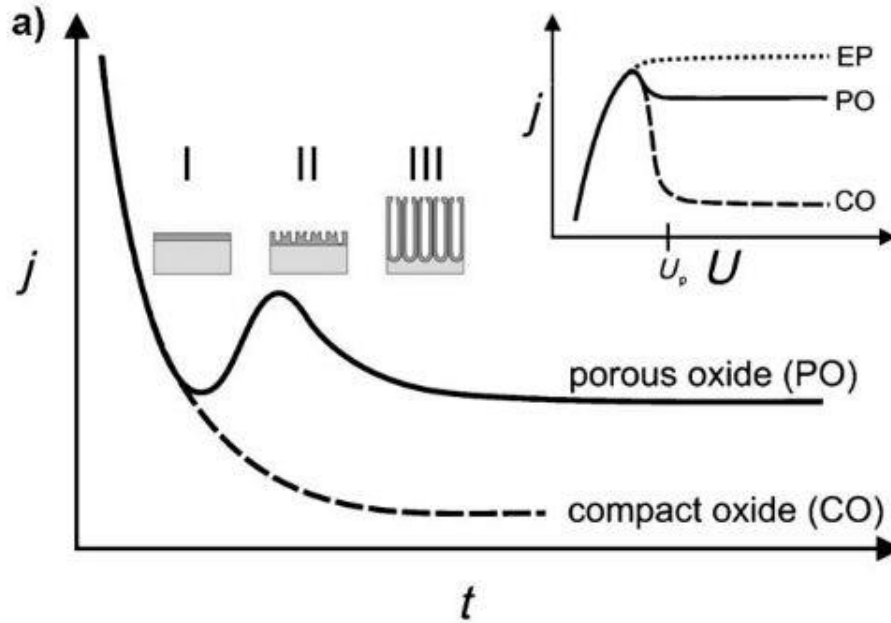


Figure 2.5 : Electrical behavior and ion transport during anodization [13]: (a) Current-time transient in the presence (solid line) and absence (dashed line) of fluoride, (b) Field-assisted transport of ions during anodization in a fluoride-free electrolyte, (c) Field-assisted transport of ions during anodization in a fluoride-containing electrolyte.

Porous anodization of titanium can be divided into three generations according to the fluoride sources and solvents of the electrolyte. As the fluoride source and solvent change, different growth behavior and limit thicknesses are observed and attributed to the electrolyte's pH and viscosity [21,22]. First-generation titania nanotubes grown in acidic HF containing aqueous electrolytes have a limited thickness of 500 nm because of the aggressive nature of the electrolyte. [56,57]. When the growth rate of nanotubes is balanced with the chemical dissolution rate, the film thickness reaches its limit and does not increase anymore, as shown in Figure 2.6.

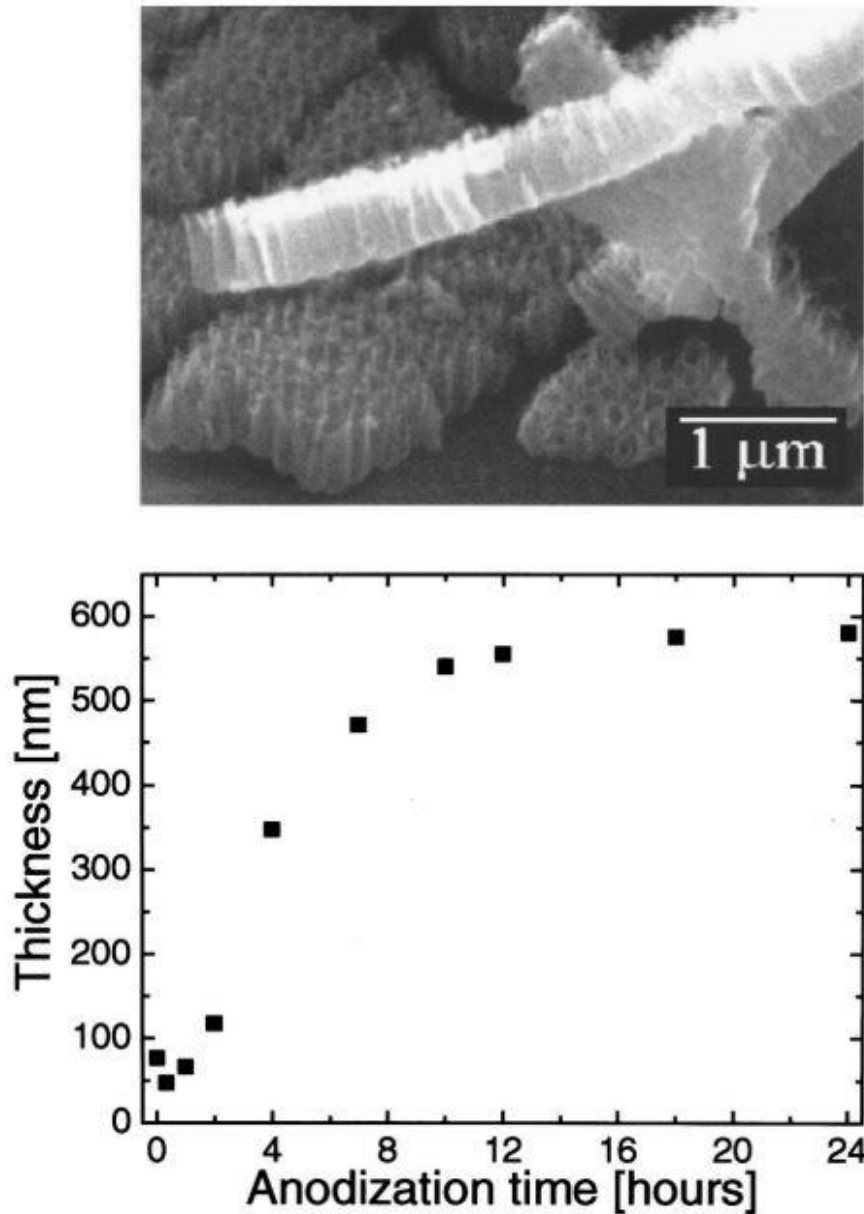


Figure 2.6 : SEM image and thickness – time graph of nanotubes grown in HF-based electrolyte [57].

Second-generation titania nanotubes produced in buffered (neutral), aqueous solutions of fluoride salts (NH_4F , NaF) also have a limited thickness up to several microns. The electrolyte's relatively higher pH allows the formation of longer nanotubes compared to anodization conducted in an acidic medium [22]. On the other hand, third-generation titania nanotubes that are grown in neutral organic solutions (i.e., glycerol or ethylene glycol) may have a thickness in the range of hundreds of microns as the high viscosity of the organic electrolytes reduces ion migration and results in lower local acidification and dissolution caused by fluoride ions [25,58,59].

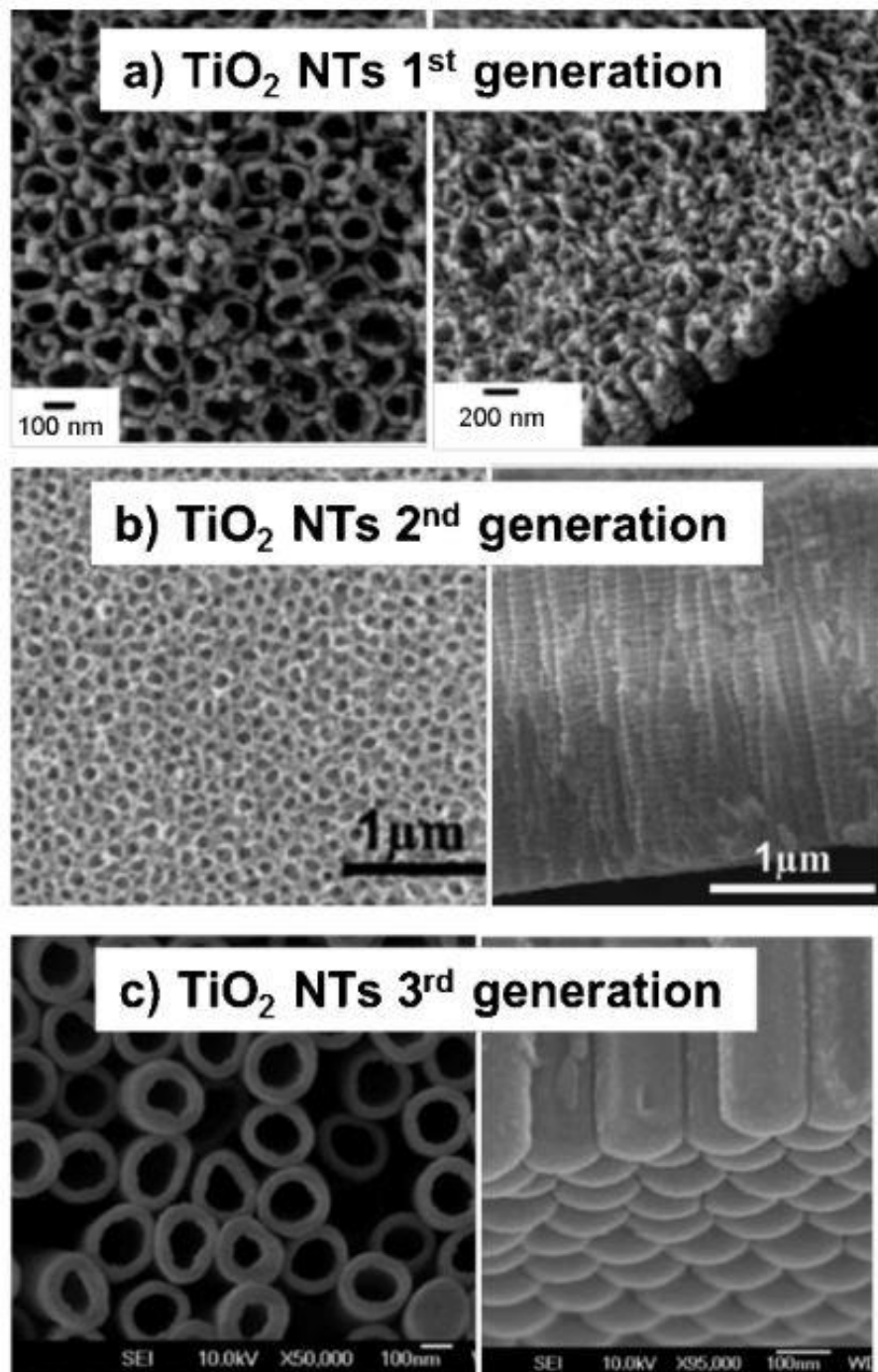


Figure 2.7 : Generations of TiO_2 nanotubes [19].

Paulose et al. reported over 1000 μm thick titania nanotube film (longest reported) by anodization in ethylene glycol solution containing NH_4F and water (0.4 wt % NH_4F , 2.5 vol % H_2O in E.G. anodized at 60V for 168h) [60]. Today studies have been mainly focused on the anodization in these types of organic electrolytes (most commonly NH_4F and a small amount of H_2O in ethylene glycol), and with fine-tuning of conditions, titania nanotubes with various sizes, shapes, and morphologies have been obtained [9,14].

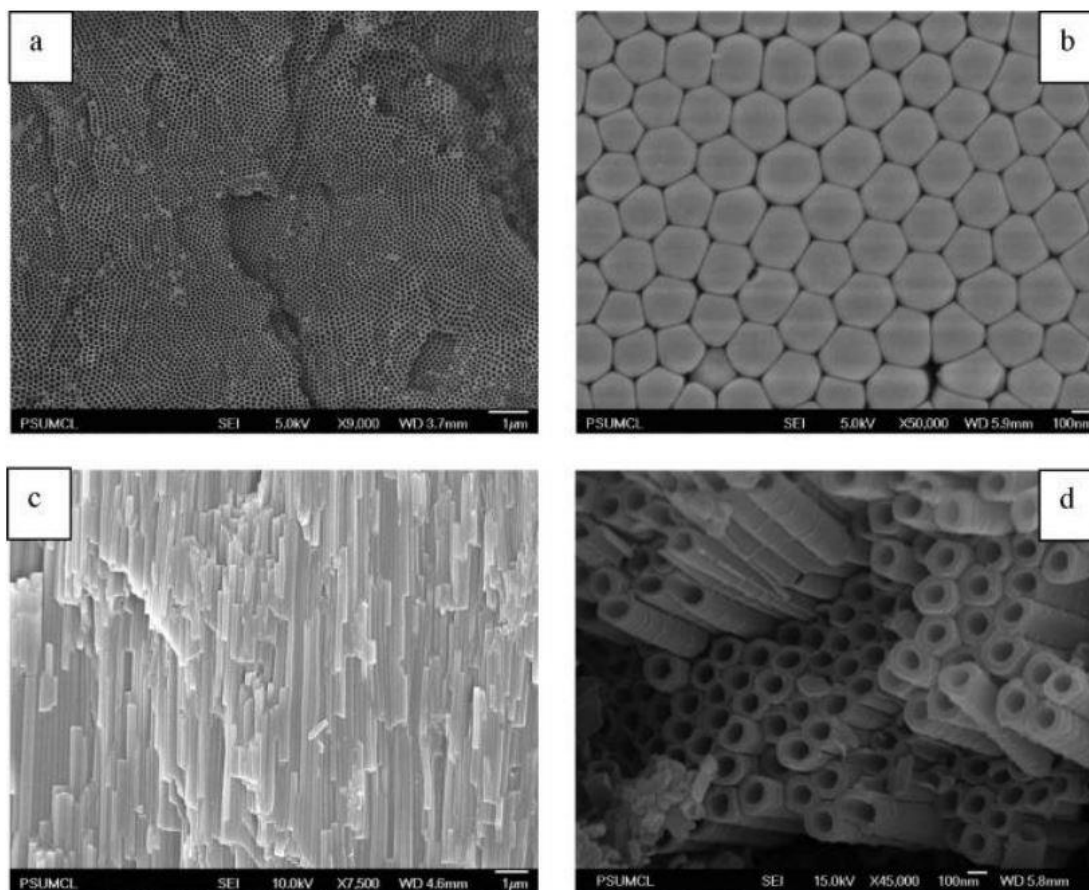


Figure 2.8 : TiO₂ nanotube morphology grown in ethylene glycol based electrolyte [60]: (a) Top side view, (b) Back side view, (c) Cross-section view, (d) Tilted view.

Besides the typical nanotubular structures, several advanced TiO₂ nanotube geometries have been achieved by varying anodization parameters. For instance, bamboo-shaped nanotubes (Figure 2.9(a)) are produced by pulsed voltage during anodization. Pulsing time and used voltages determine the size and distances of the bamboo rings [61]. The water content of the electrolyte also has a significant effect on the formation of bamboo-shaped nanotubes [62]. Branched nanotubes (Figure 2.9(d)) have been produced by applying voltage steps during anodization. As the voltage has a major effect on the size of the nanotubes, branching becomes possible under suitable conditions [61]. Double-walled nanotubes (Figure 2.9(e)) are obtained by anodizing in a suitable organic electrolyte at high voltage resulting in an inner carbon-rich shell inside the tube wall. After annealing, the carbon-rich shell is decomposed, leaving a double-walled structure with a higher surface area [63]. Formation of double-layer nanotubes (Figure 2.9(f)) are based on sequential anodization under different conditions to achieve application-specific functional properties [64,65].

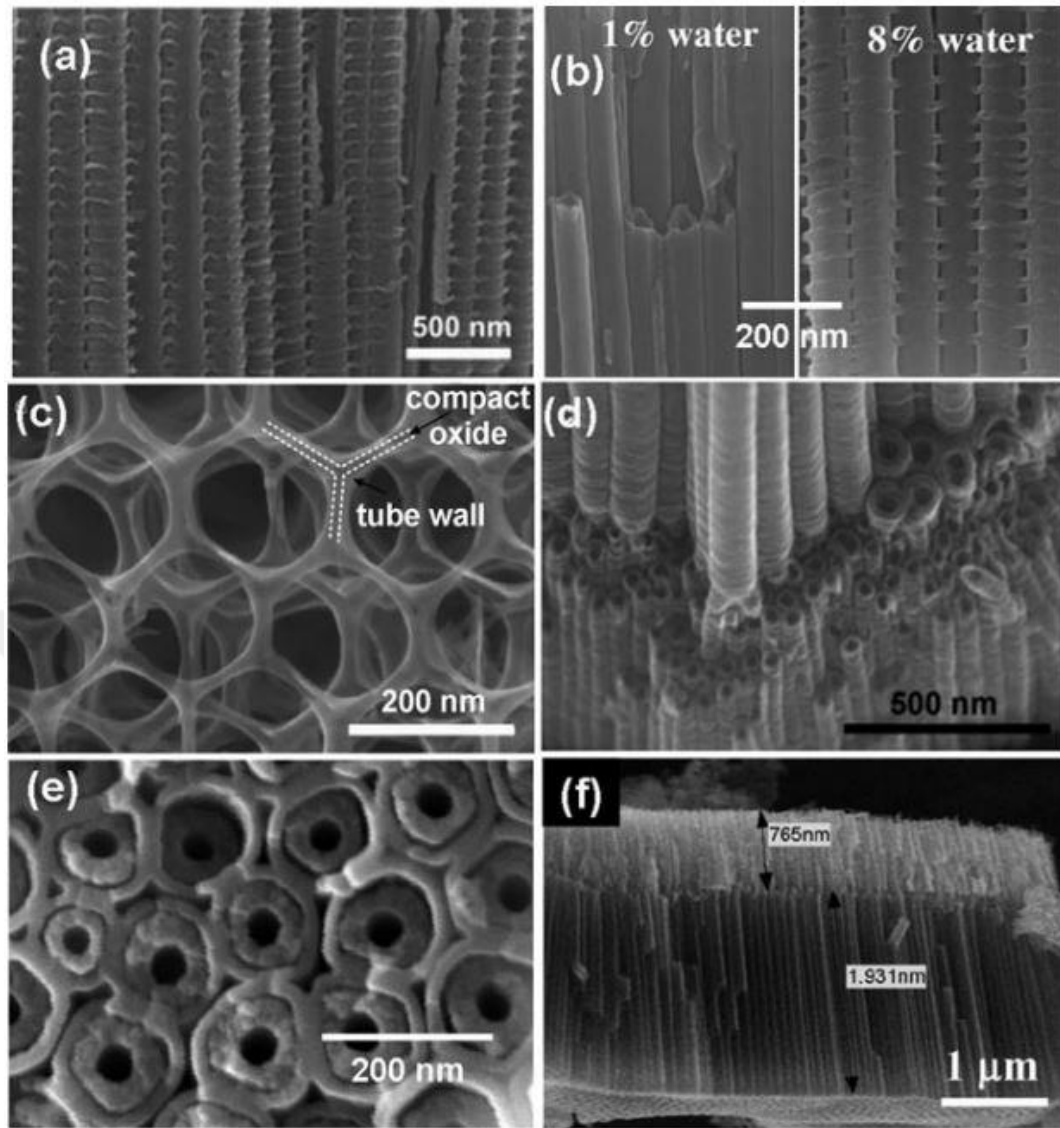


Figure 2.9 : Examples of advanced titania nanotube morphologies [13]: (a) Bamboo shaped nanotubes, (b) Smooth to bamboo-shaped transition, (c) Nanolace, (d) Branched nanotubes, (e) Double-walled nanotubes, (f) Double-layer nanotubes.

2.4 Parameters Affecting the Titanium Anodization

Major anodization parameters and their effects on anodization are well-studied. As described in previous sections, electrolyte composition and properties such as fluoride source, solvent type, pH, and viscosity significantly affect the regularity of the tubes and the final thickness limit of the nanotube arrays. Neutral organic-based anodization electrolytes are frequently used in recent anodization studies. Fluoride and water concentration in the electrolyte are the main parameters that determine the characteristics of the solution. On the other hand, major process parameters such as anodization potential, temperature, and time critically impact the growth, final

structure, and morphology. Besides, several other parameters such as roughness of the sample, stirring, and electrolyte condition also has distinct effects on the growth process of the nanotubes.

2.4.1 Electrolyte composition

Ethylene glycol-based anodization electrolytes are typically used for producing third-generation titania nanotubes. Electrolytes are generally composed of NH_4F and a small amount of water dissolved in ethylene glycol solvent. The amounts of fluoride and water in the solution significantly affect the nanotube growth process.

Fluoride concentration in the anodization electrolyte has a strong relationship with the current density as the fluoride concentration increases in the electrolyte, anodization current density increases inverse logarithmically, as shown in Figure 2.10.

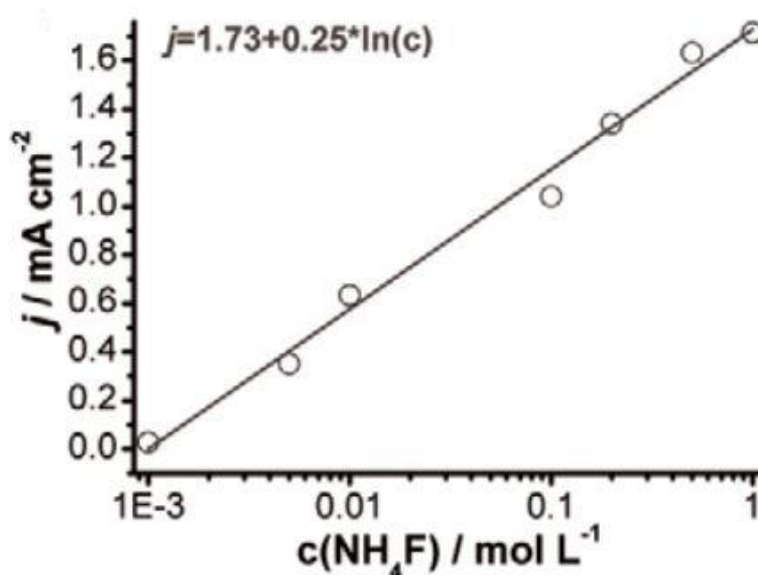


Figure 2.10 : Anodization current density versus fluoride concentration [66].

An increase in the current density also indicates a higher nanotube growth rate. As shown in Figure 2.11, higher fluoride concentration results in thicker nanotube film in anodization performed for equal durations [67]. On the other hand, as the fluoride ions are the main reason for the formation of soluble $[\text{TiF}_6]^{2-}$ species, the fluoride concentration significantly affects the electrolyte's chemical dissolution power; and on the nanotube growth. When the fluoride content of the electrolyte increases, the efficiency decline caused by chemical dissolution begins earlier during the anodization [66]. It is also reported that a higher concentration of fluoride in the electrolyte results

in the earlier formation of disordered top layers during anodization [66]. While chemical dissolution becomes very dominant at high fluoride concentrations, the growth rate remains very low at low fluoride concentrations. Therefore, it is favorable to use moderate fluoride concentrations in anodization electrolytes.

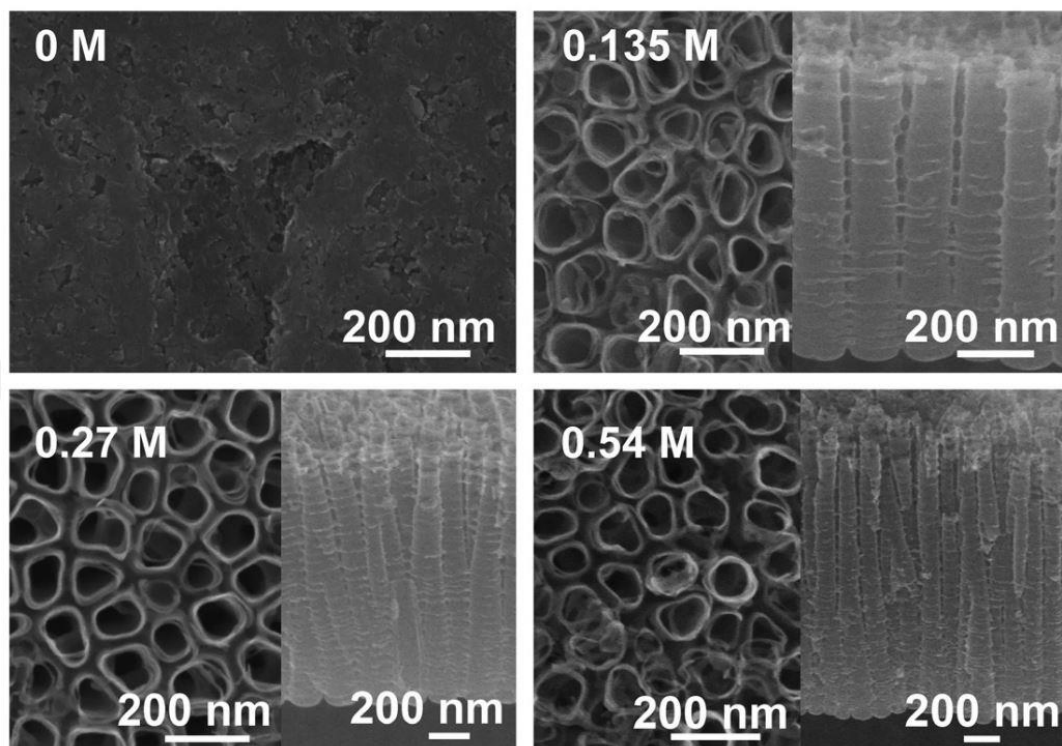


Figure 2.11 : Effect of fluoride concentration on morphology and film thickness (anodized at 20V for 3h in water/glycerol electrolyte) [67].

The water concentration in the ethylene glycol-based anodization electrolyte has a mild influence on pH and a substantial effect on the conductivity of the electrolyte. An increase in water concentration in the solution causes a decrease in conductivity [68]. Anodization studies at different water concentrations showed that electrolytes containing water in the range of 1-3% exhibit the highest current density during anodization [66]. It is possible to obtain titania nanotubes in an ethylene glycol electrolyte containing water higher than 0.18 wt % [69]. As nanotubular formation is not seen at low water concentrations (lower than 0.18 wt %), high water concentrations (higher than 13 wt %) lead to the formation of a sponge-like structure [66]. A moderate water concentration level (i.e., % 1 to % 5) is appropriate to obtain ordered nanotube structures.

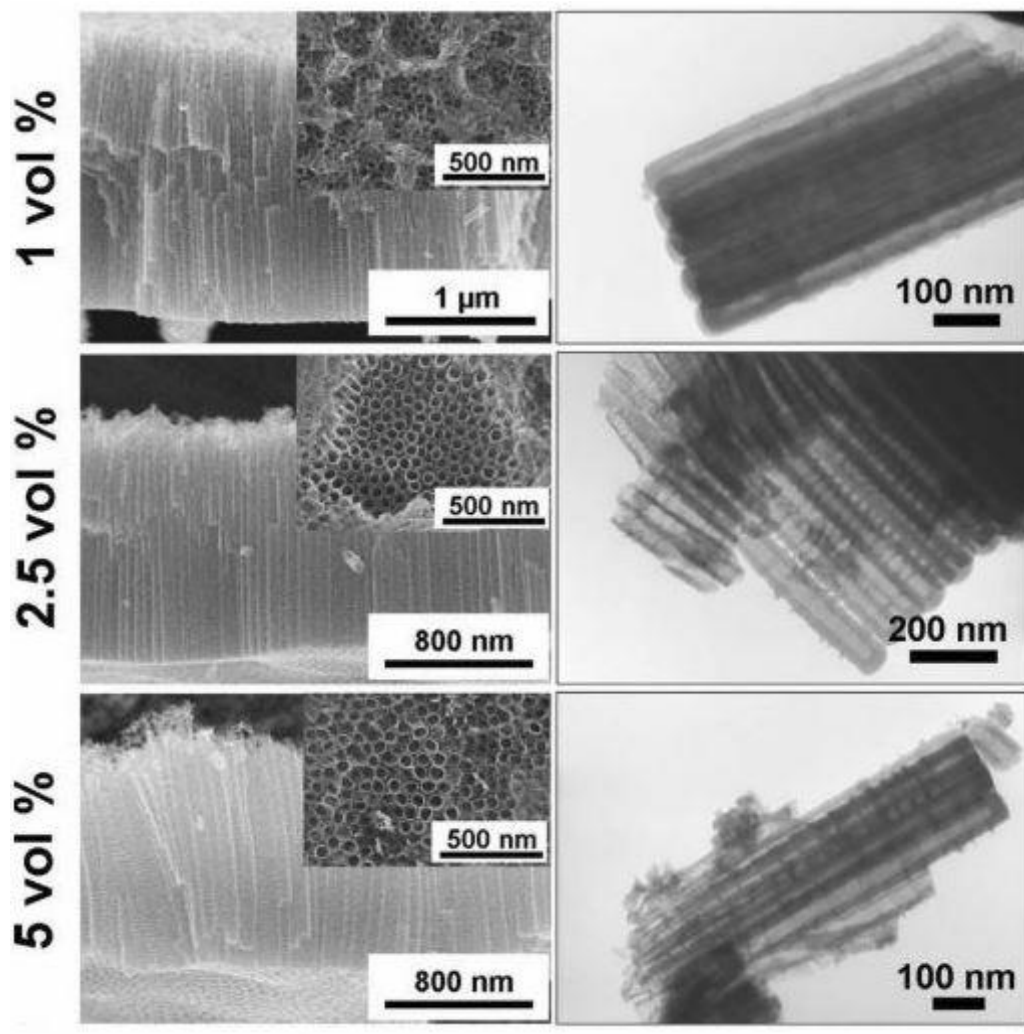


Figure 2.12 : Examples of titania nanotube structures obtained by anodization in glycerol electrolyte containing different water concentrations [68].

2.4.2 Anodization voltage

The anodization voltage has significant effects on the growth process of the nanotubes. Firstly, anodization voltage strongly affects the growth rate of the nanotubes. The increase in voltage causes the anodization current density to increase, thus increasing the nanotube growth rate as the growth rate of the nanotubes is linearly dependent on the electric load passing through the system [70]. Another remarkable effect of the anodization potential is on the tube diameters. Smaller diameter tubes can be obtained at low anodization potentials, while tube diameters increase at higher anodization potentials [71].

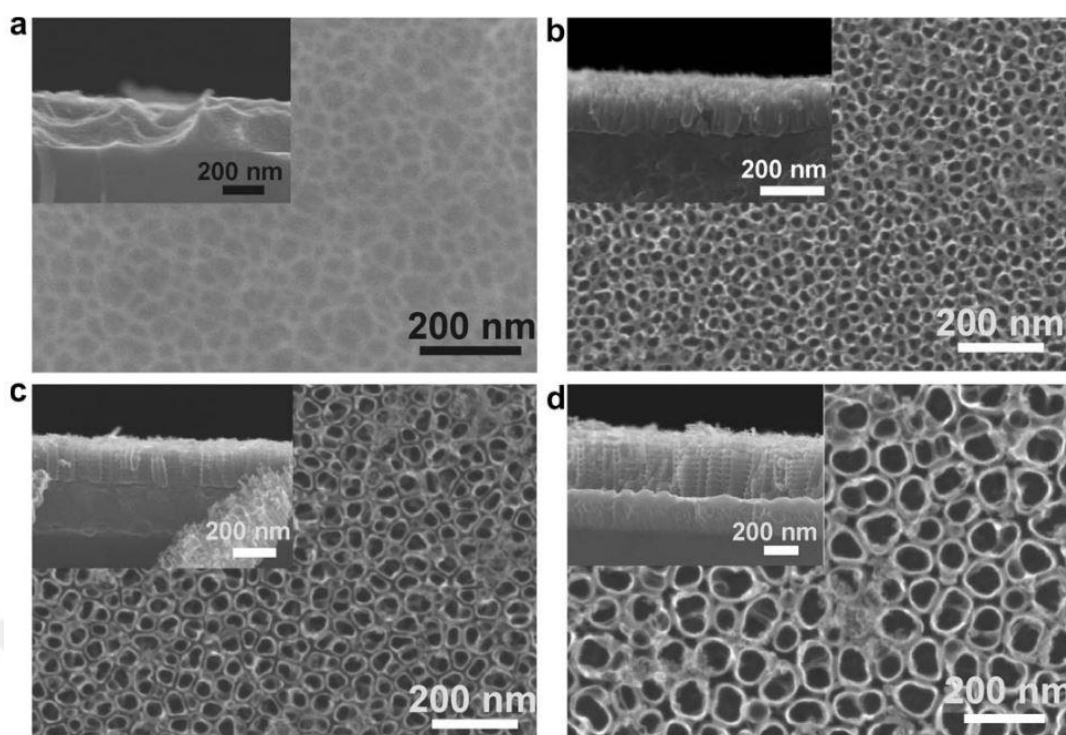


Figure 2.13 : SEM images of anodization conducted in 1M H₂SO₄ / 0.15 wt % HF at different potentials (1st generation nanotubes) [71]: (a) 1 V, (b) 5 V, (c) 10 V, (d) 20 V.

The nanotube diameters increase linearly with increasing voltage, generally in a range of 2-3 nm.V⁻¹ in ethylene glycol-based anodization electrolytes [66]. Another critical point is the impossibility of nanotube formation at lower and higher potential values than a specific range, depending on the anodization electrolyte type and composition. While a minimum potential is needed for nanotube formation, the breakdown of the tubes occurs at higher potentials than a limit potential [66]. For ethylene glycol-based anodization electrolytes, while anodization voltages below 5 V are not sufficient for efficient nanotube formation, it not practical to produce TiO₂ nanotubes at higher potentials than 60V, as the breakdown potential corresponds to values around 60-90 V depending on the electrolyte composition. At potential values above the breakdown voltage, electropolishing of the surface starts to occur instead of anodization [66,72].

For titanium anodization in ethylene glycol-based electrolytes, 20 to 60 V potentials are suitable for producing titania nanotube with constant efficiency. Higher potential values are advantageous as they provide a higher growth rate. Besides, it is known that higher anodization potential values within the formation potential range are more beneficial in terms of the ideal ordering of the nanotubes [73].

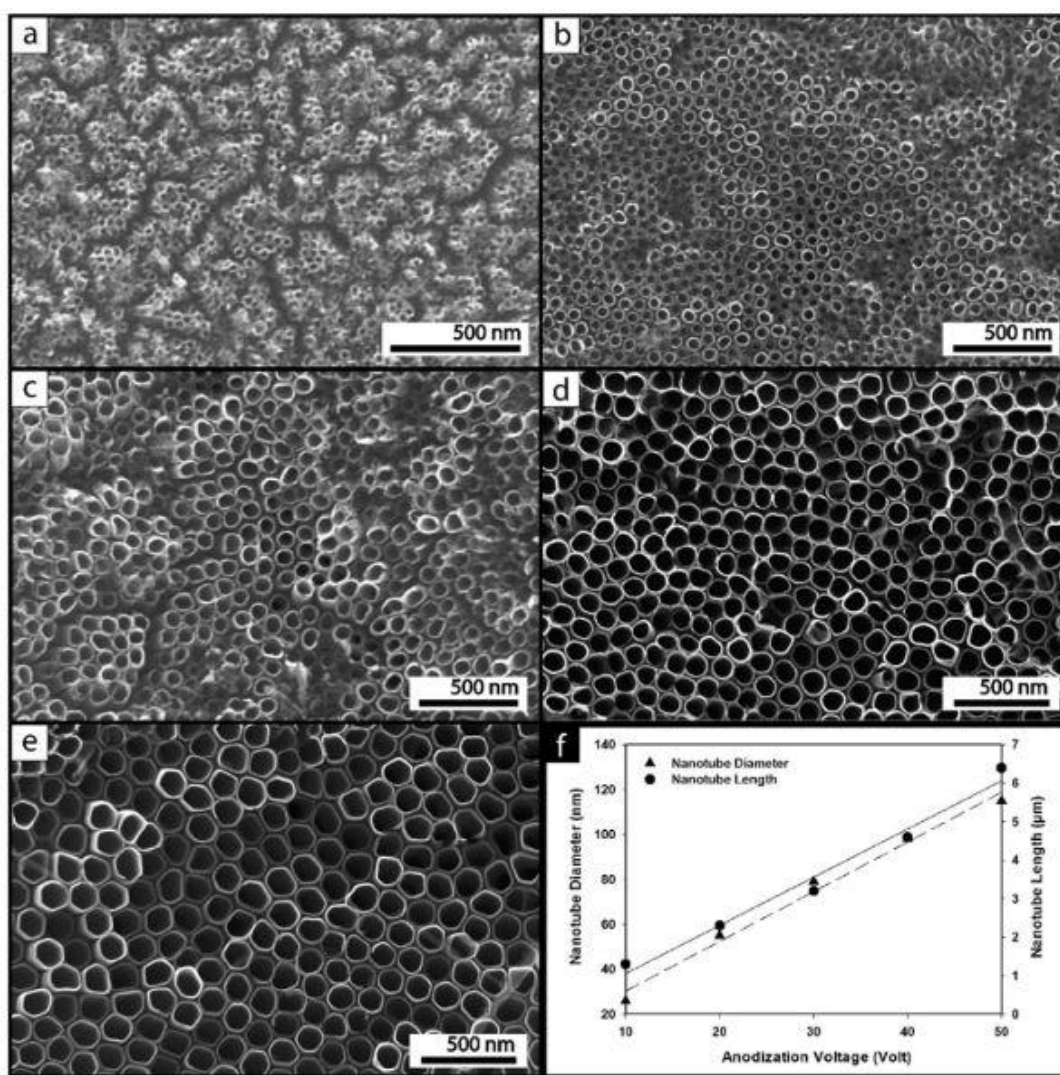


Figure 2.14 : SEM images of anodization conducted in 0.4 wt % NH_4F , 5 wt % H_2O (in E.G.) at different potentials (3rd generation nanotubes) [74]: (a) 10 V, (b) 20 V, (c) 30 V, (d) 40 V, (e) 50 V, (f) Diameter and length versus potential graph.

2.4.3 Anodization temperature

The anodization temperature has a complex effect on the anodization process. Increasing temperature causes higher mobility of the ionic species, increasing anodization current density, thereby enhancing field-assisted growth. However, on the other hand, with increasing temperature, the rate of chemical dissolution also increases significantly, which has a negative effect on the growth rate of nanotubes [37,75].

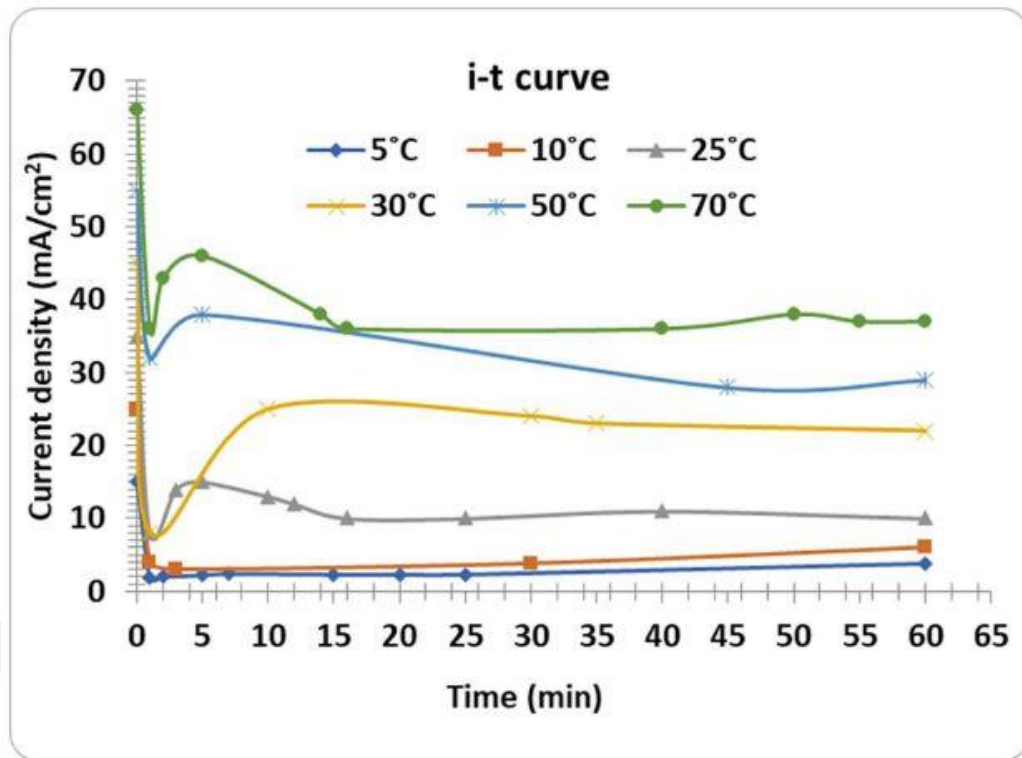


Figure 2.15 : Effect of anodization temperature on the current density (anodization at 30 V in HF-based electrolyte) [75].

Although there are complicated current density behaviors in the early stages of the formation process, the effect of temperature on the anodization current density is observed after the growth and dissolution processes become balanced (Figure 2.15). The increase in temperature causes the ion mobility and diffusion rates to increase, and the F^- and O^{2-} ions in the electrolyte reach the electrolyte-oxide interface and oxide-metal interfaces faster, accelerating the growth process (oxidation and dissolution) [75].

A significant increase in the chemical dissolution rate occurs with the increase in anodization temperature. The increased chemical dissolution rate cause earlier dissolution and degradation of the nanotubes, resulting in irregular tube morphologies after anodization [37]. On the other hand, although low temperatures make it easier to control chemical dissolution, it causes inefficient and low growth rates due to low current density. In addition, the anodization temperature has a mild effect on the nanotube pore diameters [25]. As the anodization temperature increases, a slight increase in the nanotube diameters is observed (Figure 2.16).

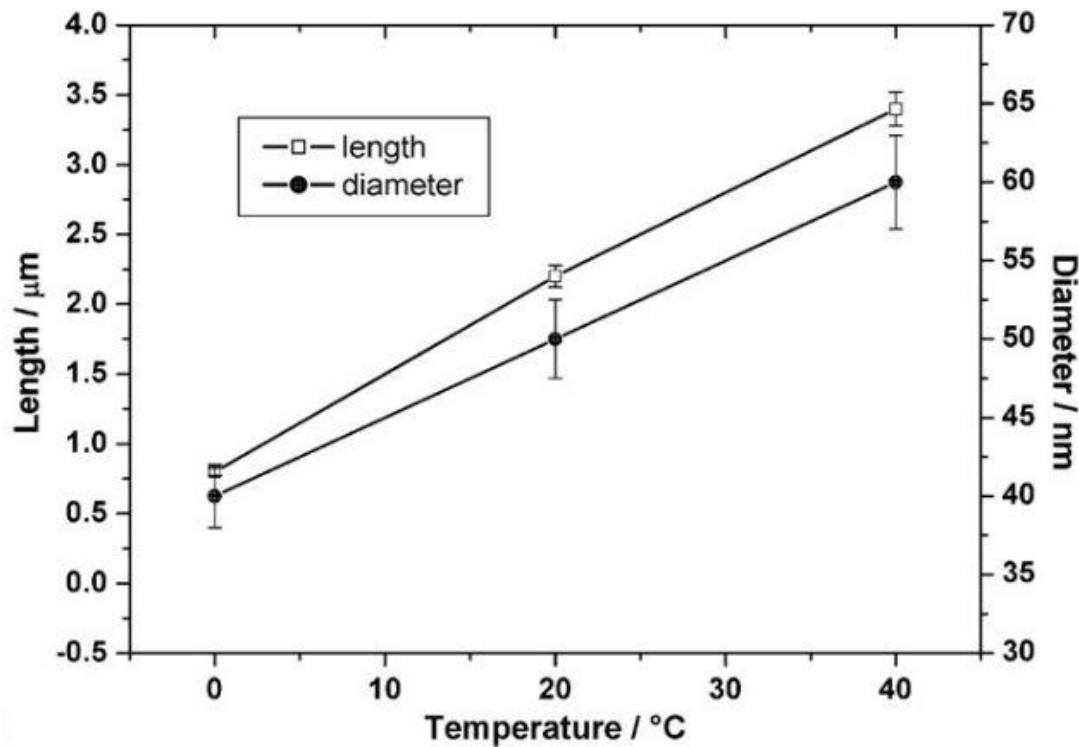


Figure 2.16 : Effect of anodization temperature on diameter and length of nanotubes anodized in glycerol electrolyte [25].

2.4.4 Anodization duration

Anodization duration is the primary parameter determining the final length of the nanotubes. As the nanotube length is dependent on the electric load passing through the system, longer anodization durations lead to longer nanotube film [70].

As the nanotube film gets thicker, the resistance of the film increases, resulting in the gradual decrease of the anodization current density. In a typical anodization process, the current decreases as long as the nanotube film becomes thicker. As the anodization progresses, the current density decrease rate gradually slows down, and the current-time graph begins to flatten, as shown in Figure 2.17 [48].

Although the current density value varies according to many parameters such as the anodized material, anodization electrolyte, voltage, temperature, the current density trend shows a decreasing characteristic as the nanotube film gets thicker [48].

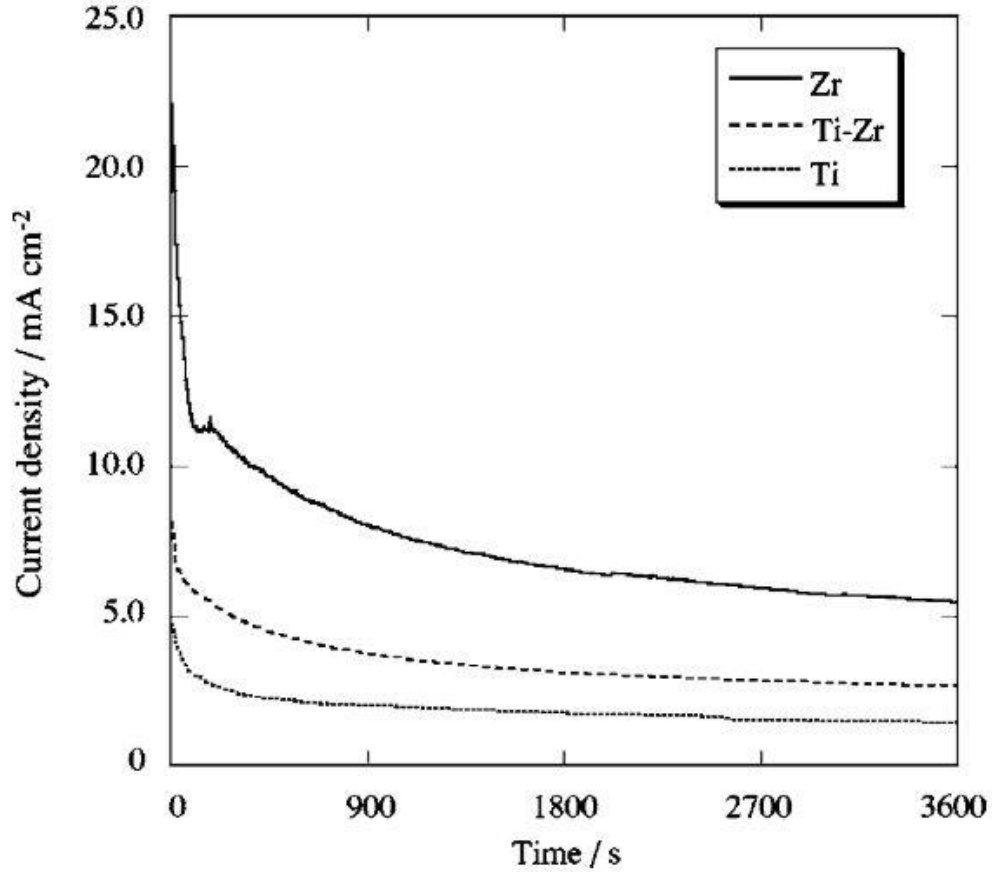


Figure 2.17 : Current-time graph of Ti, Zr and Ti-Zr during anodization at 20V in 1M (NH₄)₂SO₄ + 0.5 wt % NH₄F (aqueous) electrolyte [48].

Later during the anodization, the effects of chemical dissolution surge with the disintegration of so-formed protective surface layers. Once the chemical dissolution of the formed nanotubes becomes dominant, growth efficiency declines, causing thickening of the film to decelerate and stop completely at some point. Even though time is the significant parameter determining the nanotube film thickness, after a certain period of anodization time, which depends on the solution type, the nanotube growth rate decreases to a very low level or completely stops [57]. In 1st generation (HF-based) and 2nd generation (aqueous fluoride salts) electrolytes, cessation of growth may occur within minutes or hours. Anodization durations more extended than this point do not increase nanotube length. In 3rd generation (glycerol/ethylene glycol-based) electrolytes, cessation of growth may occur in days [25,57]. The time-dependent tube length graph (Figure 2.18) shows the deceleration and cessation of nanotube growth in 2nd and 3rd generation electrolytes [25].

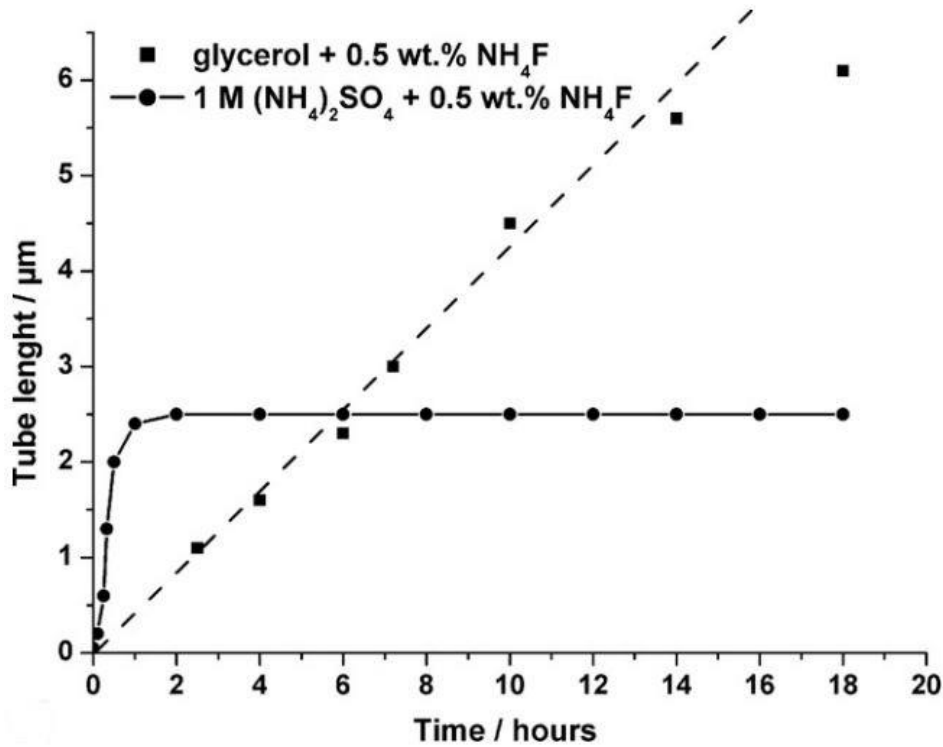


Figure 2.18 : Effect of anodization duration on nanotube growth behavior during anodization in different types of electrolytes (2nd generation vs. 3rd generation nanotubes) [25].

2.4.5 Other parameters affecting the titanium anodization

Several other parameters, such as roughness of the sample, stirring, and electrolyte condition, strongly influence the anodization process.

2.4.5.1 Stirring rate

Since anodization is conducted in liquid electrolytes, stirring can be expected to be an important parameter. There are few studies investigating the effect of stirring on the anodization process. Young-Taeg et al. reported that the increase in stirring speed causes the anodic formation voltage to decrease during the anodic oxidation of titanium in sodium hydroxide. They suggested two different explanations for this observation: i) removing attached gas bubbles from the anode surface by sufficient agitation; ii) disintegration of the electrical double layer consisting of ions on the oxide/electrolyte interface, which acts as an electrical barrier [16]. In addition, Narayanan and co-workers investigated the effects of stirring on anodization by performing anodization experiments with and without agitation under the same conditions. Although a specific rpm value was not specified in the study, it is seen that the current density is lower in the agitated anodization condition. They reported that

the stirring during anodization increases the tube length at 20 V, but it has no effect at 30 V and 40V [76].

Moreover, Syrek et al. investigated the effect of stirring during titanium anodization (0 to 500 rpm) on the growth process of nanotubes. A downward trend in current densities was observed as the stirring speed increased. They also reported increasing stirring speed during anodization results in thicker nanotube films. However, they found that as the stirring speed increased, the nanotube lengths were shorter than the expected theoretical lengths, and this was attributed to the increased chemical dissolution rate due to stirring. They also noted that, while no remarkable effect is seen up to 300 rpm, a decrease in pore diameter, cell size, and porosity is observed at higher stirring speeds [77].

2.4.5.2 Surface roughness

The effect of surface roughness on the titanium anodization process has been studied in several works. Apolinario et al. applied different pre-treatments (chemical etching, mechanical polishing, and electropolishing) to titanium foils before anodization and investigated their effects on the growth process. They observed that while chemical etching increases the R_q value, mechanical polishing and electropolishing significantly decrease the R_q value of the titanium sample. They reported that the surface smoothness of the sample has a significant effect on the nanotube growth process, and the samples with lower R_q values showed an increased growth rate and better degree of ordering under identical anodization conditions [78]. Recently, Asgari and co-workers suggested a new electropolishing technique for Ti foil for better surface smoothness; and they employed the surface-improved structures in anodization to examine its effects on growth. The polished samples produced in the study contain nano-sized ripple-like structures with low R_q values. They reported that lower R_q values lead to a higher growth rate, and the ripples on the surface act as pore formation points promoting growth and ensuring the formation of highly ordered structures [79]. In addition to surface polishing techniques, the two-step anodization technique is also used to produce highly ordered nanotube structures. In this procedure, the surface is first anodized, and then the formed nanotubular oxide film is peeled off, leaving a regular pit array on the surface. The pits are pore formation points and ensure a highly-ordered nanotube structure during second anodization [80].

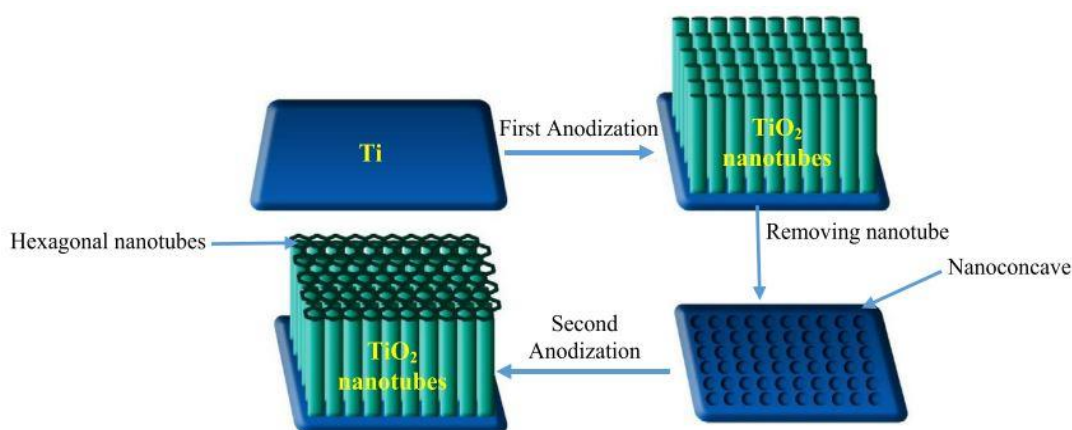


Figure 2.19 : Schematic representation of double anodization [80].

2.4.5.3 Aging and reuse of the anodization electrolyte

The aging or reuse of the ethylene glycol-based electrolytes affects the anodization process in several ways. It is well known that F^- ions are consumed during the anodization of titanium. Jarosz et al. conducted a study investigating the behavior differences of clean and aged (used) ethylene glycol-based anodization electrolytes. It has been reported that aged electrolyte leads to decreased growth rate and shorter nanotubes, attributed to the decreased oxidation rate due to reduced F^- ions in the electrolyte. The reduction of F^- ions in the electrolyte causes a decrease in the electrolyte conductivity and the anodization current density [81]. Few additional findings were obtained in different studies conducted on aged ethylene glycol-based electrolytes. Sopha et al. investigated the behaviors of 0 - 50 hours aged ethylene glycol-based electrolytes and observed that nanotube formation was inhibited in long-aged (50 hours) electrolytes due to depletion of fluoride ions in electrolytes [82]. Gulati et al. investigated the effects of 1 - 10 hours of aged ethylene glycol-based electrolytes on the anodization process. Besides many common findings, they observed that aged electrolyte affects the mechanical stability of the formed nanotubes and indicated that nanotubes fabricated in 10 hours aged electrolyte was mechanically more robust and more stable [83]. Guo et al. conducted anodization experiments in fresh and 10 to 30 hours aged ethylene glycol-based electrolytes and reported that nanotubes produced in aged electrolytes are mechanically more stable and have fewer cracks. They also added that, although the uniformity of the nanotubes increases in 10 to 20 hours aged electrolytes, excessive aging (more than 20 hours) causes uniformity decrease [84]. Surprisingly, in the studies of Gulati et al. and Guo et al., it was reported that higher current densities are seen in aged electrolytes, which is inconsistent with other studies.

Costa et al. reused the ethylene glycol-based anodization electrolyte 3 times in a row and investigated the differences of the 2nd and 3rd use with the clean solution. They mentioned that reuse of the electrolyte has a negative effect on the growth rate as the solution becomes acidified during repeated use, leading to the increased chemical dissolution of the tube tops [85]. Suhadolnik et al. investigated the effects of repeated usage of ethylene glycol electrolytes on the photocatalytic activity of the titania nanotubes. In this study, a total of 20 anodization experiments (1 per day) were performed with the same electrolyte, and it is observed that repeated use of the same anodization electrolyte results in shorter nanotubes lengths under the same anodization conditions. It was reported that the pH of the electrolyte increases, and the conductivity of the electrolyte decreases after each repeated anodization as the free fluoride ions decrease in the electrolyte. They also mentioned that reproducible TiO₂ nanotube arrays could not be produced in batch anodization cells due to the aging of the electrolyte [86].

2.5 Growth and Morphology of TiO₂ Nanotubes

Porous titania films' growth stages can be followed by current time behavior under constant anodization voltage. At stage I, a barrier oxide layer is immediately formed on the surface before pore initiation, and a sharp decay on the current is observed. This oxide layer has the same structure as the barrier layer observed during titanium anodization in fluoride-free solutions [26]. At stage II, fluoride ions in the electrolyte stimulate the pitting in the oxide layer (pore initiation), and an increase in the anodization current is seen as the resistance of the anodic film decreases [27]. This current increase seen in stage II is apparent in many electrolyte compositions, but it may not be present or can be very small to be seen in low water containing 3rd generation electrolytes (Figure 2.21) [68]. At stage III, nanotubes begin to grow from the initiated pores and the current enters a gradual decline period as the nanotubular oxide film thickens [28]. As more current passes through the system, the porous film thickness increases with time. In the extended anodization durations, a disordered top layer (nanograss) may form on the surface of the nanotubes. Nanograss layer is not preferred in many applications because of its irregular and loose structure [29].

The current-time graphs of the anodization performed in 2 different electrolytes are shown in Figure 2.20. The growth stages can occur within minutes in one electrolyte

(i.e., NaF/H₂O), and it may take hours in the other electrolyte (i.e., NaF/Glycerol). In addition, in some electrolyte and anodization conditions, these stages may not be seen clearly (Figure 2.21).

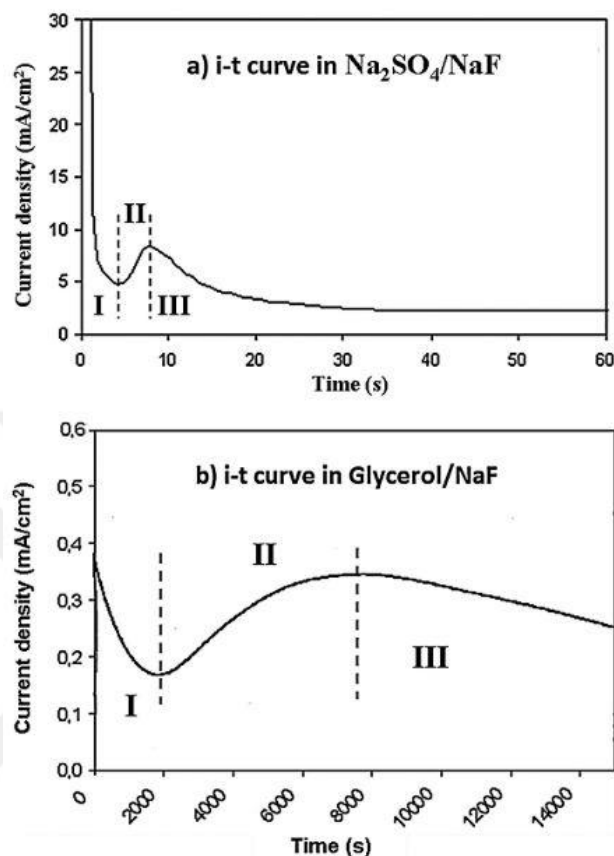


Figure 2.20 : Stages of current-time transient during titanium anodization [19].

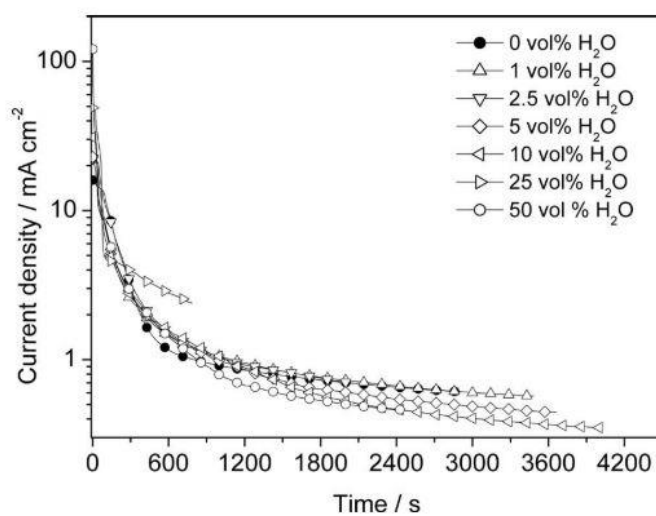


Figure 2.21 : Current-time transient of 0 - 50 vol % H₂O and 0.2 M NH₄F containing glycerol electrolyte [68].

In the titanium anodization process, chemical dissolution also significantly influences growth, aside from electrochemical oxidation and selective dissolution of the oxide. At the tube base, field-assisted oxidation and dissolution allow the nanotubes to grow into the metal. On the other hand, chemical dissolution occurs in regions other than the tube base. The chemical dissolution inside the tube on the tube walls is one of the most critical factors determining the nanotubes' inner diameter. Macak et al. demonstrated the chemical dissolution of the inner tube walls in their work. It is seen in the cross-sectional SEM images taken from the bottom, middle, and top layers of the nanotubes that the inner diameter of the tubes expands as tubes are scanned from the bottom to the top. The main reason for this difference is that the previously formed regions are exposed to the electrolyte for a longer time and undergo more chemical dissolution [73].

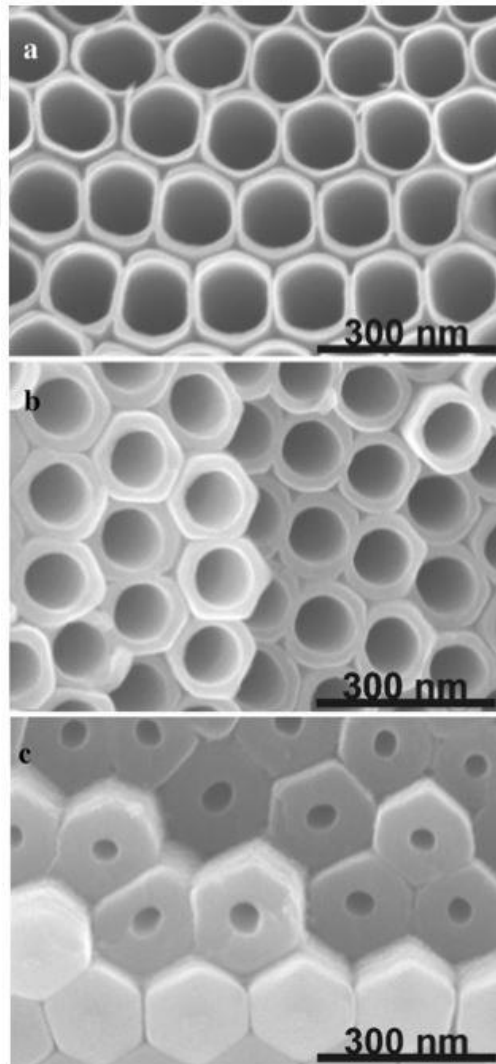


Figure 2.22 : SEM images showing (a) top, (b) middle, (c) bottom layer of the nanotubes [73].

In cases when the sample is exposed to the electrolyte for a long time (extended anodization duration to obtain longer nanotubes), chemical dissolution of the nanotube tops occurs, and a dispersed nanograss structure forms on the surface. It is an unfavoured structure in most studies as it is an irregular layer covering nanotubes' surface [29]. As the open surface and long nanotube films are the desired structures in most studies, various studies have been conducted to prevent the formation of this layer or remove it after it has formed. Examples of undesired nanograss structure (a-c) and barrier oxide-top structure (d-f) are seen in Figure 2.23.

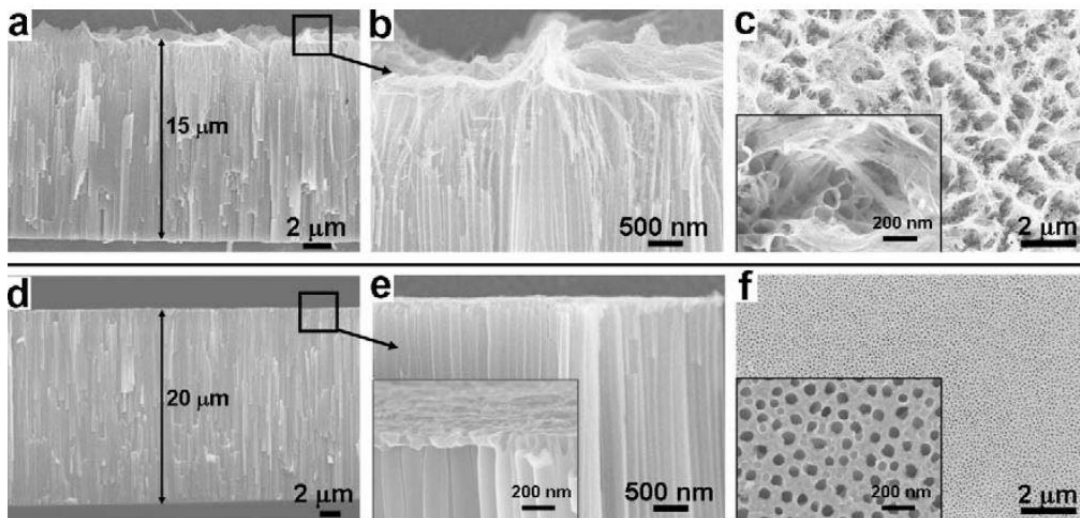


Figure 2.23 : SEM images showing nanotube layers produced on non-polished (a-c) and polished (d-f) Ti by anodization in ethylene glycol-based electrolyte under same conditions [29].

Some studies have shown that longer nanotubes without nanograss can be obtained by protecting the top layer of the nanotubes, which is attributed to restricted chemical dissolution of the nanotubes due to limited contact with the electrolyte. Kim et al. and Song et al. obtained longer nanotubes without nanograss by retarding chemical dissolution with a prior thin protective rutile film grown on the specimen via polishing and heat-treatment, respectively [29,30]. Albu et al. achieved the same progress by coating a semi-permeable photoresist before anodization, allowing ion migration and tube growth but acting as a resistance to chemical etching and protecting the tube tops [31]. Some groups studied to suppress nanograss formation by tuning anodization conditions such as water content of the electrolyte [32], the addition of organic additives [33], changing the viscosity of the electrolyte [34]. On the other hand, in several other studies, so-formed nanograss structure was cleared by ultrasonication [35] or stripping with scotch tape [36], which can severely damage nanotube films.

2.6 Growth Model of TiO₂ Nanotubes

To explain the formation of nanotubular structures on titanium, the field-assisted dissolution model that is developed initially for aluminum has been extensively used. According to this model, tubular film growth is controlled by the balance between field-assisted formation of oxide at the metal-oxide interface and the dissolution of the oxide at the oxide-electrolyte interface (tube bottoms) [87]. Even though this growth model had been used for decades, in some cases, it was not adequate to explain abnormal volume expansions during titania nanotube formation. A different growth model, the field-assisted flow, was proposed to consider this volume expansion in recent years. In this model, it is proposed that the volume expansion and resulting stress that occurred during field-assisted growth is relieved by the plastic flow of the oxide. According to this model, the oxide formed at the tube bottom moves upwards by the flow mechanism to form nanotube walls [48,88,89].

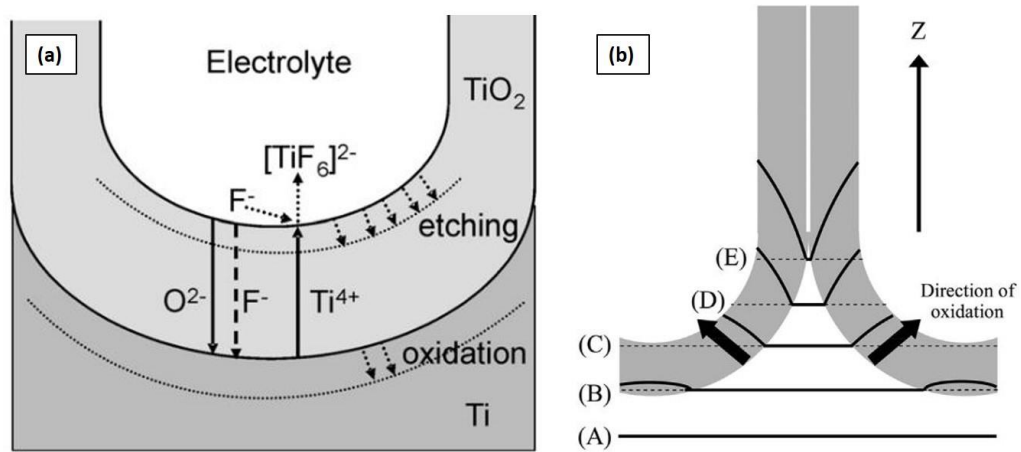


Figure 2.24 : Schematic representation of growth models for TiO₂ nanotubes: (a) Field-assisted dissolution model [18], (b) Plastic flow model [48] Lines (A-E) show the movement of Ti atoms (Dashed lines – initial position, solid lines – final position).

Besides, small-sized fluoride ions migrate through the tube bottom oxide layer twice as fast as oxygen under the effect of the electric field and accumulate at the outer part of the oxide, forming a fluoride-rich layer (FRL). This layer also moves upwards by the oxide flow and forms the fluoride-rich outer wall, as shown in Figure 2.25 [90]. The common opinion about the transition from nanopores to nanotubes is the high dissolution tendency of this fluoride-rich layer (FRL) located at the pore junctions (triple point) and outer part of the tube walls which is also well-supported by the flow model [90].

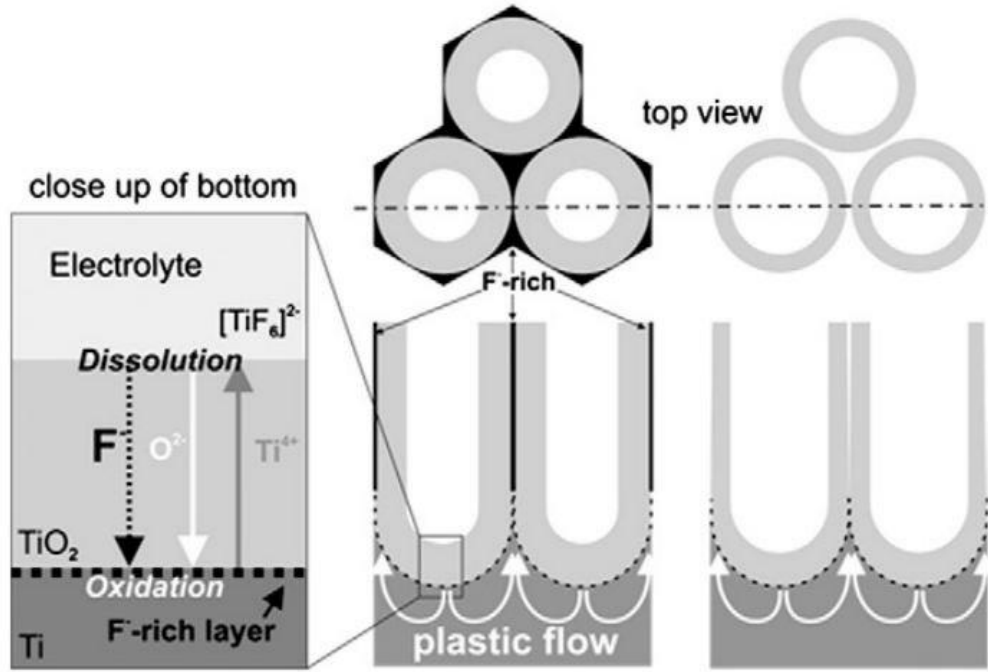


Figure 2.25 : Schematic representation of fluoride rich layer (FRL) formation [90].

2.7 Titanium Anodization Kinetics

The kinetics of nanotube formation and growth has been investigated by using different techniques and approaches. Xie et al. investigated the effect of fluoride concentration, temperature, and applied potential on nanotube formation. They suggested a model for simulating optimal growth conditions (fluoride concentration and temperature) for nanotube formation [37]. Butail et al. investigated nanotube growth rate versus temperature and voltage. They found that nanotube growth rate increases exponentially with temperature under constant voltages. The results supported that nanotube growth is thermally activated and obeys the Arrhenius equation [38]. Cortes et al. suggested a mathematical model for the growth of titania nanotubes with variables including voltage, fluoride, and water concentrations and time; and tried to verify the model with the experimental data taken from the literature. Even though the model showed consistency with some data sets, it gave a very high error ratio in others [39]. Zhang et al. conducted a systematic study investigating time-dependent final nanotube lengths at different temperatures and voltages and observed a linear dependence at all anodization temperatures. They also reported that temperature dependence of the nanotube lengths follows the Arrhenius relationship, with a linear activation energy-anodization potential relation [41]. Suliali et al. studied anodization reaction kinetics and produced a model for simulating anodic current

during anodization. They tested and verified the model at different anodization potentials and NH_4F concentrations. They reported that anodic current increases with anodization potential and NH_4F concentration, and it is the integral function of the water quantity during anodization [47].





3. EXPERIMENTAL PROCEDURE

Ti foils (99.6% purity, 0.050 mm) were cut into pieces of 15 mm x 25 mm size, cleaned by ultrasonication for 10 minutes in acetone, deionized (DI) water, and ethanol in sequence, and were dried by air blowing.

All electrolyte preparations and anodization processes were performed inside a glovebox (Mbraun Labstar, $\text{H}_2\text{O} < 1\text{ppm}$, $\text{O}_2 < 1\text{ppm}$) to eliminate moisture absorption of the electrolyte and maintain the reproducibility of the results. The electrolyte temperature was precisely controlled ($\pm 0.1\text{ }^\circ\text{C}$) by external water circulating thermostat connected to a double-walled stainless steel tank placed inside the glovebox. Anodization experiments were carried out inside a polypropylene container close fitted inside the double-walled stainless steel tank. Anodization current and temperature were recorded continuously during the anodization. All anodization electrolytes were prepared from high purity chemical reagents (Ethylene Glycol – Merck 99.5% assay; NH_4F – Merck 98% assay) and ultra-pure water.



Figure 3.1 : The image of the anodization system inside the glovebox.

All anodization experiments were performed using a two-electrode configuration, in which Ti foil was used as the anode and stainless steel plate (30 mm x 50 mm) was used as the cathode. The distance between the anode and cathode was kept at 2 cm.

In the first part of the experimental studies, an investigation of the effects of minor and major anodization parameters and optimization of the anodization conditions were

carried out. During these studies, anodization experiments were performed in ethylene glycol solution containing NH_4F (0.6 wt %) and H_2O (1 vol %).

In order to investigate the effect of two-step anodization conditions on surface roughness, untreated titanium foils anodized in the fresh electrolyte by applying 50 V at 30 °C for different durations (15 min to 180 min) and characterized by FESEM and profilometer after anodization. Effects of stirring rate on anodization process were investigated in the range of 0 to 1000 rpm by conducting anodization at different voltages (50 V to 60 V) and temperatures (20 °C to 30 °C) for 20 minutes, and optimized stirring condition was determined. The electrolyte was mechanically stirred at the optimized value (750 rpm) by a magnetic stirring bar (2 cm) in subsequent anodization experiments. The aging and reuse of the electrolyte were investigated in terms of its effects on current density, growth rate, and morphology by conducting repeated anodization experiments under 50V at different temperatures (10 °C to 30 °C) and durations (20 min to 180 min). Effects of repeated use of electrolytes on the nanotube morphology were determined by FESEM characterization.

Subsequently, the effects of the major parameters (voltage temperature, time) on the morphology were investigated by performing anodization at several voltages (40 V to 60 V) and temperature ranges (10 °C to 40 °C) for different durations (5 min to 180 min); and characterized by FESEM.

In addition, ultrasonication and stripping with tape methods were tested to remove the surface residues on several samples. The results were evaluated before and after stripping with FESEM.

In the second part of the experimental studies, the formation and growth kinetics studies were carried out using the reproducible conditions optimized in the first part. Fabrication of the nanotubes was conducted by the two-step anodization method. In the first anodization step, samples were anodized by applying 50 V in an ethylene glycol solution containing NH_4F (0.6 wt %) and H_2O (1 vol %) at 30 °C for 3 hours, which was optimized in the previous studies. After anodization, the samples were immersed in deionized (DI) water and ethanol in sequence and were dried in nitrogen blow inside the glovebox. After the drying process, the sample was taken out of the glovebox and ultrasonicated in ethanol to remove the anodized film.

For the second anodization step, the samples were cleaned with the previously mentioned procedure. The back and edges of the samples were masked with cellulosic lacquer for ensuring an identical active anodization area ($\sim 1.75 \text{ cm}^2$). After masking, samples were dried overnight and placed inside the glovebox for the second anodization. At the second anodization step, electrolytes were prepared freshly and used only once for each experiment. Anodization experiments were conducted by applying 50 V in an ethylene glycol solution containing NH_4F (0.3 wt %) and H_2O (1 vol %) at different temperatures (-5°C to 35°C) for different durations. After anodization, the samples were immersed in deionized (DI) water and ethanol in sequence and were dried in nitrogen blow inside the glovebox. After the drying process, the samples were taken out of the glovebox for characterization.

Surface roughness measurements of the Ti foil were conducted with a non-contact optical profilometer (Veeco Wyko NT1100). Morphology and thickness characterizations of the nanotubes were investigated using a field-emission scanning electron microscope (JEOL JSM 7000F). FESEM investigations for all samples were conducted in the middle 0.25 cm^2 region of the anodized area. Cross-sectional FESEM investigations were always conducted in the center of the anodized area irrespective of the anodization conditions.



4. RESULTS AND DISCUSSION

Many different parameters affect the structure of nanotubes formed during titanium anodization. In order to produce titanium dioxide nanotube films with the desired structure and reproducibility, it is necessary to have effective control over the anodization process and parameters. Thus, the effects of the anodization parameters on the process and the final structure were investigated by evaluating the literature data and conducting experiments in the determined parameter ranges. The parameters were optimized to obtain reproducible results in the formation and growth kinetic studies.

Ethylene glycol is a very hydrophilic solvent that absorbs remarkable moisture when left in the ambient atmosphere. The absorbed moisture content varies depending on the relative humidity and directly affects the conductivity of the solution [91]. This character of ethylene glycol causes the water content of the electrolyte to change during anodization which has a strong influence on anodization current density and nanotube morphology [69]. Therefore, anodization under ambient atmosphere causes reproducibility problems, especially in extended anodization operations. Nevertheless, anodization studies conducted under a controlled atmosphere are few among the literature's formation and growth kinetics studies. Although it is not practical to perform anodization in a controlled atmosphere (glovebox), it is essential for understanding the formation behavior and growth kinetics of the anodization process. In this study, the anodization system was installed in a glovebox, and all solution preparation and anodization processes were carried out inside the glovebox to eliminate moisture absorption of the anodization electrolyte and to ensure reproducibility.

As the anodization parameters may interfere with each other and obscure the understanding of the anodization process, the parameters other than the analyzed parameter were kept constant precisely during the study. One of the commonly used anodizing electrolyte composition ranges in the literature was employed (0.3 - 0.6 wt % NH_4F , 1 vol % H_2O , E.G.). The amount of water in the electrolyte was chosen as 1 vol %, an appropriate value for the formation of smooth nanotubes, and this value was

kept constant in all experiments. Two different fluoride concentrations were used in the experiments. In the first part of experimental studies (investigation and optimization of the anodization parameters), where numerous experiments were needed, the value of 0.6 wt % NH_4F was preferred as higher fluoride content provides a higher reaction and growth rate and allows experiments to be completed in less time. On the other hand, 0.3 wt % NH_4F was preferred in the second part of the experimental studies (formation and growth kinetics investigations) in order for the reactions and morphological transitions to occur at a slower pace due to lower fluoride content, which can be monitored fluently.

4.1 Investigation and Optimization of Anodization Conditions

In the first part of experimental studies, the effects of various experimental parameters on the anodization process were investigated and optimized.

Firstly, in order to standardize the pre-anodization surface and obtain higher nanotube quality, two-step anodization conditions were investigated and optimized. Then, the effect of the stirring rate on morphology was investigated, and the stirring rate to be used in the experiments was determined. Besides, the first (fresh) and repeated use of anodization electrolyte was studied in detail, and its noteworthy effects on current density and morphology were reported.

Secondly, after determining the operating conditions and procedures to be used in the experiments, the effects of voltage, temperature, and time parameters on morphological transformations were investigated, and remarkable findings were obtained, which helped explain the formation and growth process of the nanotubes.

In addition, although not widely used, some experiments on the removal of surface residues by using scotch tape and ultrasonication were carried out, and the results were evaluated.

4.1.1 Optimization of two-step anodization procedure

The regularity of the nanotube structures obtained by titanium anodization is significantly affected by the pre-anodization surface condition of the sample. Mechanical, chemical, and electrochemical polishing methods have been utilized to ensure surface smoothness. It has been reported that while the chemical method has a

negative effect, the mechanical and electrochemical method has a positive effect on the roughness of the surface [78]. On the other hand, it is also known that two-step anodization is an effective method to obtain a well-organized nanotube film. In this method, preliminary anodization is performed, then the resulting film is removed from the surface, and the sample is anodized again. As a result of removing the oxide film formed in the first anodization, footprints of the tube base (dimples) remain on the sample surface. These dimples act as starting points in the second anodization step and improve the regularity of the final nanotube structure [80]. Although the two-step anodization is widely used in the studies, the characteristics of first anodization that determine the pre-anodization surface condition have not been sufficiently studied. In order to observe the effect of the first anodization step on the surface roughness, the samples were anodized for different durations, then the formed oxide was cleared off and examined with FESEM and optical profilometer.

FESEM image of the untreated foil (cleaned with acetone, water, and alcohol) is presented in Figure 4.1. The image taken at 500x magnification shows that the sample surface is significantly rough, has microcracks, and contains regions (dark areas) presumed to be contaminated.

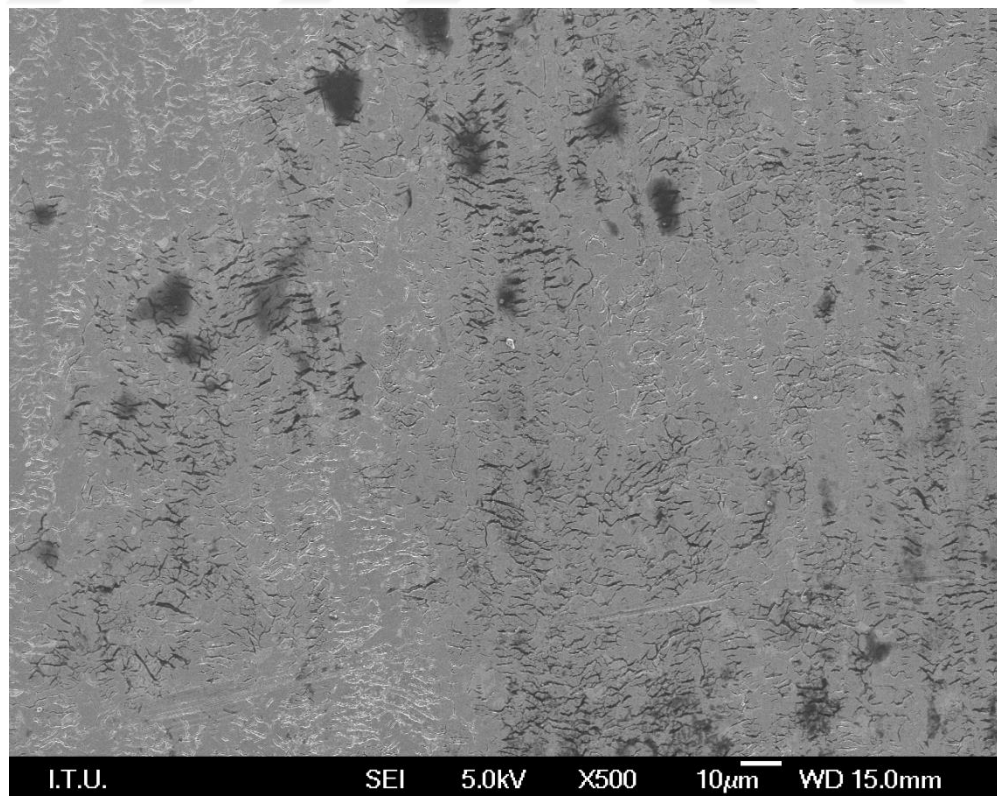


Figure 4.1 : FESEM image showing the surface condition of untreated Ti foil.

In the study, samples were anodized in a fresh anodization electrolyte (0.6 wt % NH_4F , 1 vol % H_2O , EG) under 50 V anodization potential at 30 °C for 15 min, 90 min, and 180 min. After anodization, the anodic oxide films were removed entirely from the surface by ultrasonication for 15 minutes. The FESEM images of the samples (after removal of the film) clearly show that the surface condition of the foil is highly affected by the first anodization duration.

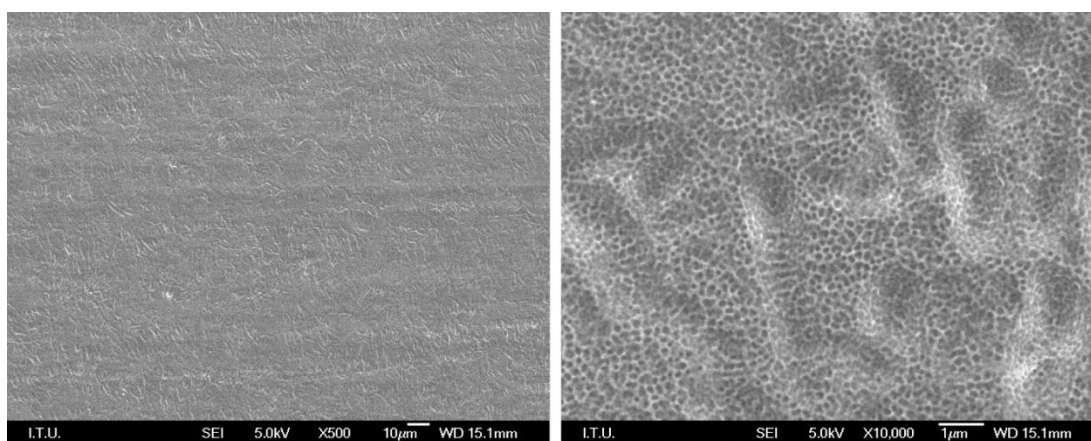


Figure 4.2 : FESEM images showing the surface condition of the sample after removing the oxide film produced by anodization at 50 V and 30 °C for 15 min.

When the sample was anodized for 15 minutes, the grown oxide was removed, the surface condition changed significantly compared to its untreated state. The nanotube base traces (dimples) of the removed nanotube film were visible on the sample surface. Besides, when the FESEM images taken at 500x magnification are compared, it can be seen that the contaminated regions on the surface have disappeared in the anodized samples. However, only a slight improvement in surface roughness was obtained with a 15 min anodization (Figure 4.2).

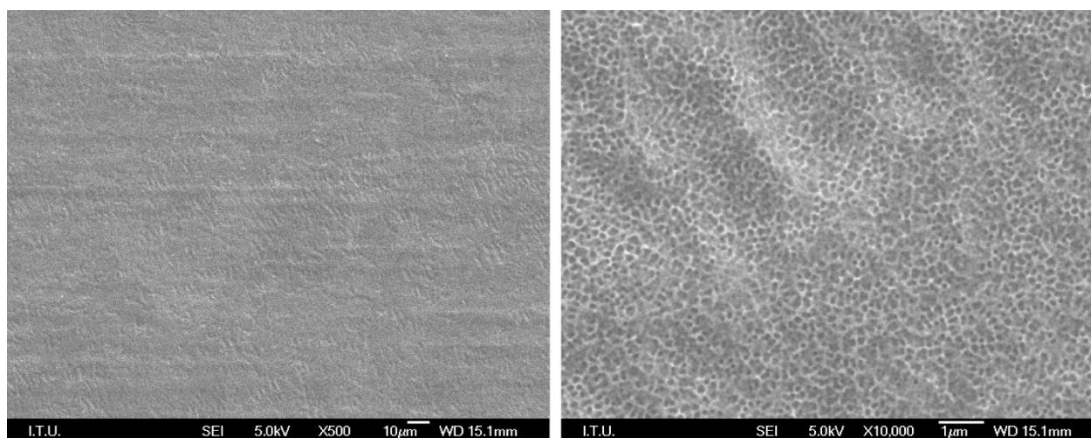


Figure 4.3 : FESEM images showing the surface condition of the sample after removing the oxide film produced by anodization at 50 V and 30 °C for 90 min.

When the anodization duration was increased to 90 minutes, and the grown oxide was removed, a moderate improvement in surface condition was obtained. Compared with the 15 min anodized sample, while the advantages of dimples and clean surfaces were preserved, surface smoothness was improved to a better level (Figure 4.3).

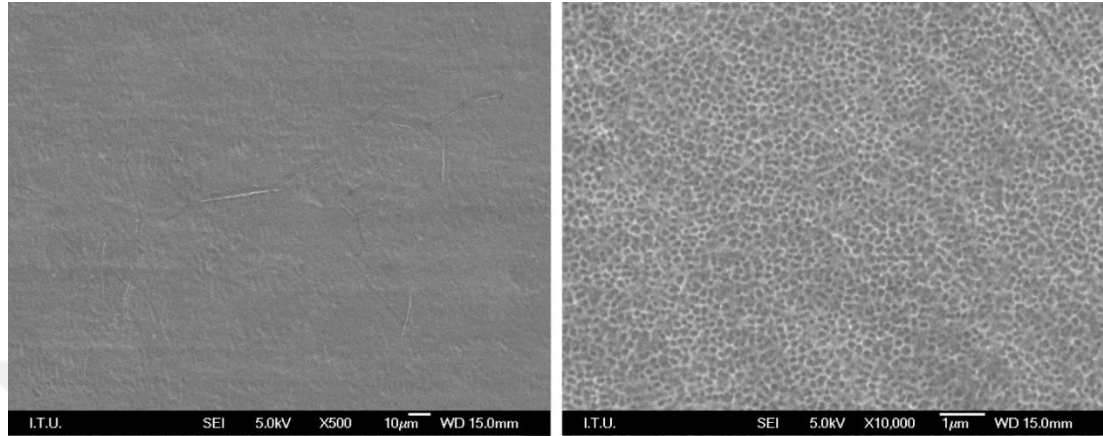


Figure 4.4 : FESEM images showing the surface condition of the sample after removing the oxide film produced by anodization at 50 V and 30 °C for 180 min.

In the case of anodizing for 180 minutes and removing the grown oxide, a significant improvement in surface condition was achieved. The surface smoothness was improved to a very high level, and a clean pre-anodization surface containing dimples was obtained (Figure 4.4).

Although short first anodization (i.e., 15 min) is sufficient for removing the contaminated top layer of the Ti foil and allowing the formation of dimples that will serve as the nanotube initiation points and enhance ordering, it does not provide a notable advantage in terms of surface smoothness. The surface smoothness is remarkably improved when the first anodization duration is extended. In lengthy first anodization (i.e., 180 min), the indentations and protrusions are gradually equalized, and the surface becomes flat, as can be seen clearly when the FESEM images are taken at 10.000x magnification are compared (Figure 4.2, Figure 4.3 and Figure 4.4). As the anodization duration increases, the wavy appearance on the surface gradually decreases, and a smoother surface is formed.

Profilometry results also support this observation. Untreated Ti foil surface and 180 min first anodized sample surface were examined with a non-contact profilometer and compared.

3-Dimensional Interactive Display

Surface Stats:

Ra: 550.43 nm

Rq: 687.76 nm

Rt: 6.90 μm

Measurement Info:

Magnification: 5.12

Measurement Mode: VS

Sampling: 1.64 μm

Array Size: 736 X 480

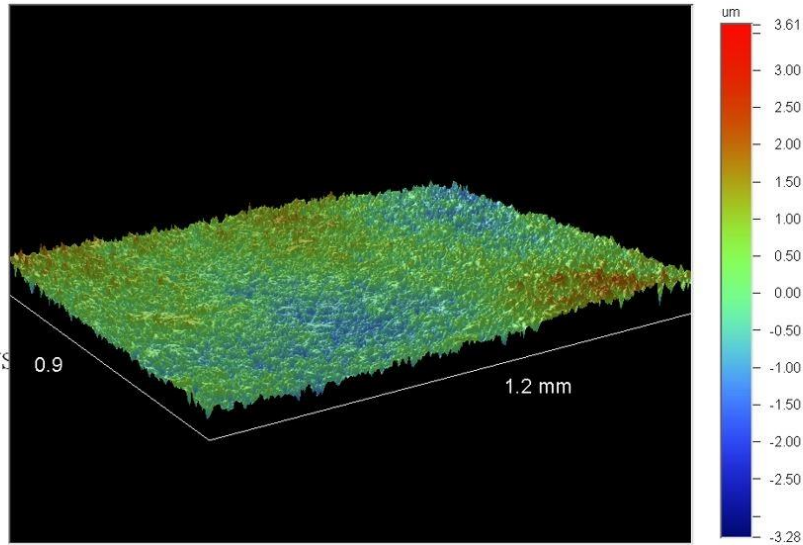


Figure 4.5 : Non-contact profilometry analysis of untreated Ti foil.

As shown in Figure 4.5 and Figure 4.6, the R_t value was decreased from 6.90 μm to 2.05 μm , and the R_a value was decreased from 550 nm to 193 nm in the 180 min first anodized sample when compared to untreated Ti foil.

3-Dimensional Interactive Display

Surface Stats:

Ra: 193.06 nm

Rq: 243.99 nm

Rt: 2.05 μm

Measurement Info:

Magnification: 5.12

Measurement Mode: VS

Sampling: 1.64 μm

Array Size: 736 X 480

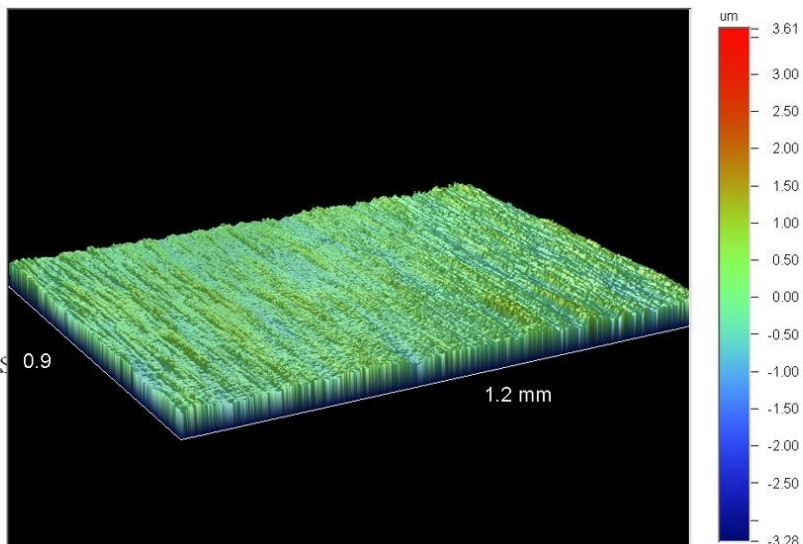


Figure 4.6 : Non-contact profilometry analysis of the sample after removing the oxide film produced by anodization at 50 V and 30 $^{\circ}\text{C}$ for 180 min.

In brief, it was demonstrated that the high surface roughness of the untreated Ti foil could be reduced significantly by the optimized first anodization procedure without utilizing any polishing procedure. Besides, with the optimized first anodization

procedure, the difficulty of applying polishing methods to 50 micron foil and creating an additional work step is eliminated. Although it may be possible to obtain a surface with a lower roughness value with an anodization duration over 180 minutes, achieved surface conditions were found to be adequate for the current study, and the optimized parameter was used in further experiments.

4.1.2 Optimization of electrolyte stirring during anodization

Agitating the electrolyte during anodization has various effects, but the number of studies on this subject is limited [16,76,77]. In these studies, the inverse effect of stirring on the current density is seen, but there are conflicting findings regarding the effects of the stirring rate on the nanotube growth process. Besides, the effect of stirring rate on morphology has not been investigated in detail. Moreover, its importance in terms of temperature control has not been mentioned. In this study, experiments on the anodization stirring rate were conducted to verify the effects of agitation described in the literature, investigate its effect on morphology and temperature control, and determine the optimized value to be used in formation and growth kinetics studies.

Firstly, in order to observe the non-stirred condition, anodization experiments were performed in 0.6 wt % NH_4F and 1 vol % H_2O containing ethylene glycol solution for 20 minutes without stirring using four different parameters: i) 60 V - 30 °C, ii) 60 V - 20 °C, iii) 50 V - 30 °C, iv) 50 V - 20 °C. As shown in Figure 4.7, there is no considerable deviation in the current density behavior of anodization experiments performed under 50 V and anodization performed at 60 V and 20 °C. However, an unusual increase in current density is depicted in the anodization performed at 60 V and 30 °C. It is seen in the figure that the decrease in the current density slows down and stops at the 200 to 300 seconds interval and starts to increase abnormally after 300 seconds. It was also determined that the anodization temperature increased in this 200 to 300 seconds interval. It was understood that the current density started to increase due to increased temperature. In addition, the increased current density accelerated the reactions and caused the temperature to increase even more. Thus, a process that current density and temperature cyclically triggered each other occurred, and both increased uncontrollably. When the anodization was conducted at 60 V and 20 °C, a slight increase in temperature was observed again. In this case, the current density and

temperature did not cyclically trigger each other. Since the temperature was kept under control with a slight deviation, the anodization current density followed the expected course. In the anodization experiments conducted at 50 V, the temperature rise during anodization remained minimal in both 20 °C and 30 °C conditions, and no unusual behavior was observed in the current-time graph.

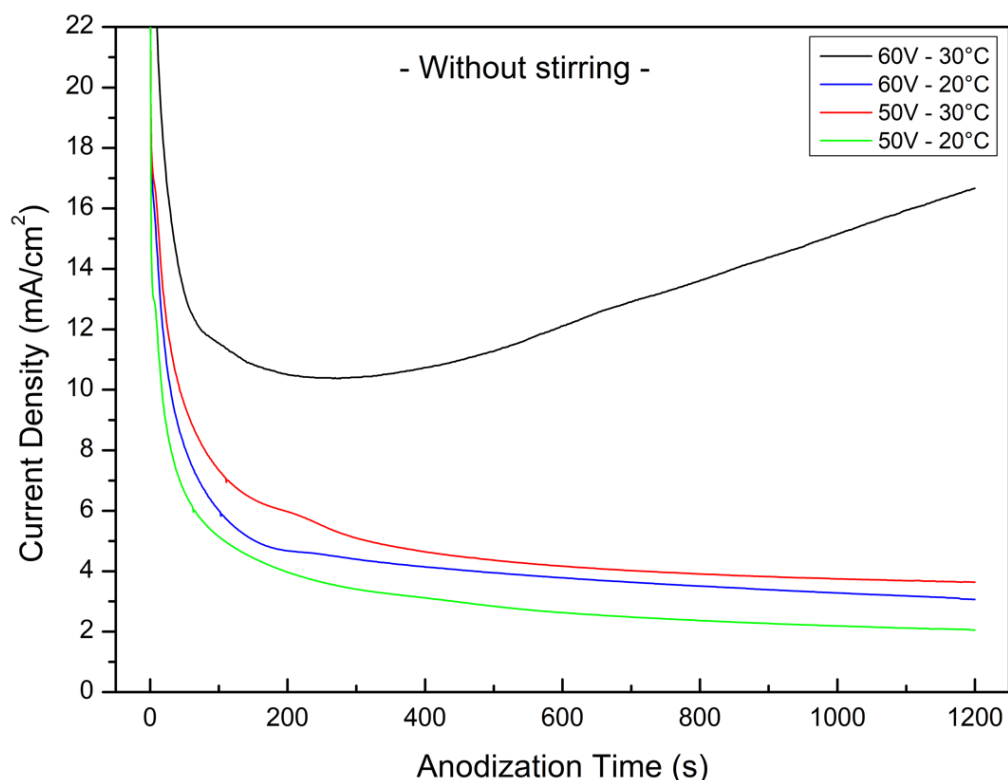


Figure 4.7 : Current density - time transient of samples anodized without stirring the electrolyte at 60 V - 30 °C, 60 V - 20 °C, 50 V - 30 °C, and 50 V - 20 °C for 20 min.

The surfaces morphology of the anodized samples was examined by FESEM analysis. It is seen that a dense nanograss layer was formed on the sample surface after anodization at 60V and 30 °C for 20 min (Figure 4.8). However, in the samples anodized at 60V and 20 °C for 20 min and 50V and 30 °C for 20 min, a hybrid surface morphology with a barrier oxide layer and open-top nanotubes was observed, as seen in Figure 4.9 and Figure 4.10, respectively. On the other hand, in the sample anodized at 50V and 20 °C for 20 min, where the voltage and temperature were the lowest, the sample surface was completely covered with the barrier oxide layer (Figure 4.11). When the current density graph and FESEM images are evaluated together, it can be observed that there is a correlation between the current density level and the morphology.

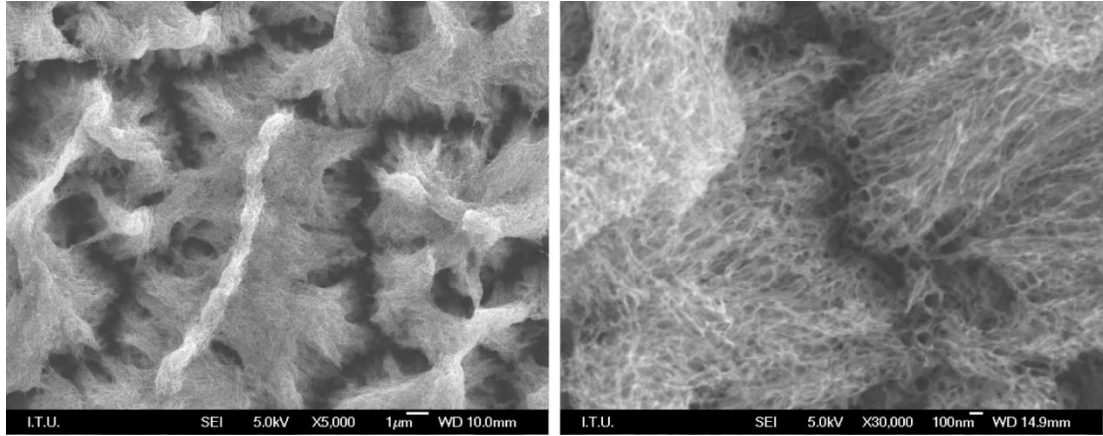


Figure 4.8 : FESEM images showing the morphology of the sample anodized at 60 V and 30 °C for 20 min without stirring.

In the sample anodized at 60 V and 30 °C for 20 min, where relatively high temperature and voltage were used, current density and anodization temperature increased uncontrollably during anodization, and chemical dissolution reached very high level with the effect of rising temperature. The formed structures (barrier oxide layer and nanotubes) dissolved and formed a dense and dispersed nanograss layer on the surface (Figure 4.8). Since the nanograss is mostly an undesirable structure, this result reveals the importance of temperature control during anodization.

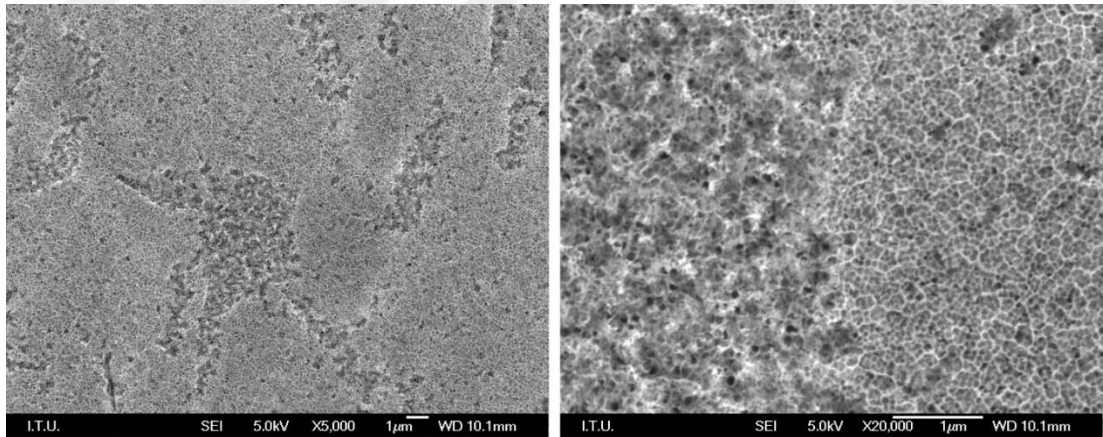


Figure 4.9 : FESEM images showing the morphology of the sample anodized at 60 V and 20 °C for 20 min without stirring.

During anodization, the temperature increase remained in the order of a few degrees for the sample anodized at 60V and 20 °C for 20 min and the sample anodized at 50V and 30 °C for 20 min. Very similar current densities and very similar morphologies were observed in these two anodization operations (Figure 4.9 and Figure 4.10).

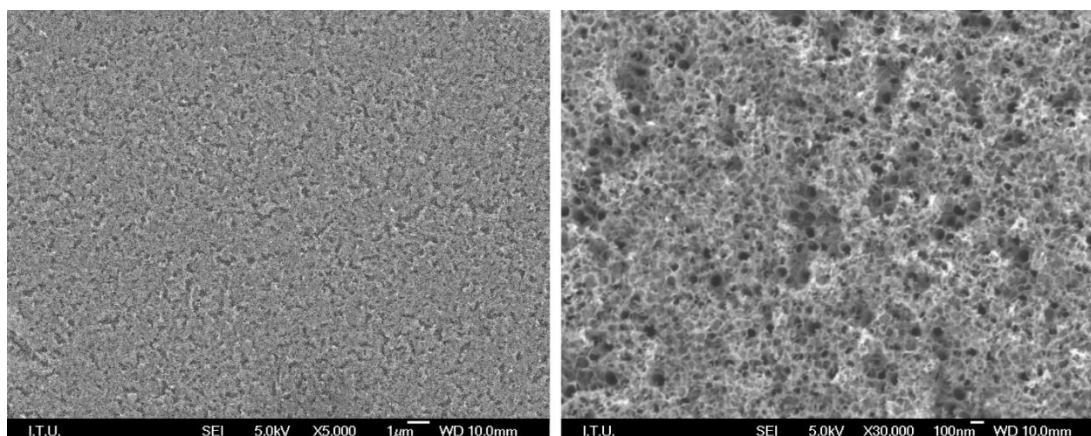


Figure 4.10 : FESEM images showing the morphology of the sample anodized at 50 V and 30 °C for 20 min without stirring.

Since the temperature did not get out of control during anodization, the typical anodization current density graph seen in the anodization process was observed (Figure 4.7). As the result of these anodization experiments, it was observed that some parts of the first-formed barrier oxide layer disappeared, and open-top nanotubes became visible through the gaps in the layer, exhibiting a hybrid morphology, as can be seen in Figure 4.9 and Figure 4.10.

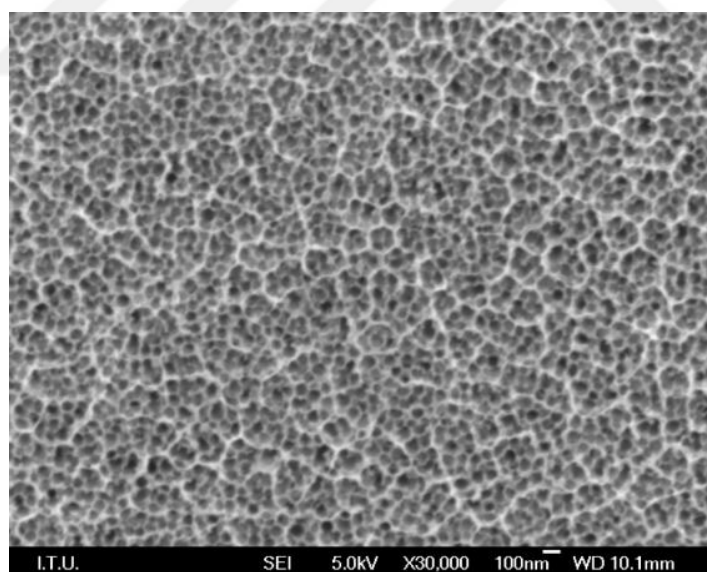


Figure 4.11 : FESEM image showing the morphology of the sample anodized at 50 V and 20 °C for 20 min without stirring.

When the anodization was performed at 50V and 20 °C for 20 min, it was observed that the surface was covered with a compact barrier layer. Surface morphology was utterly different, and there was no visible nanotube region on the surface layer (Figure 4.11). Detailed investigations on the formation of different morphologies and morphological transitions are given in the following sections.

In order to examine the effect of stirring on the temperature control, anodization at 60 V and 30 °C for 20 min was conducted in a fresh electrolyte under 1000 rpm stirring using a 2 cm magnetic bar. As shown in previous experiments, for the sample anodized at 60V and 30 °C in a stagnant solution (Figure 4.7), the temperature could not be controlled during anodization. When the stirring was added to the process, the temperature was kept under control, and the variation of the current density with time became similar to a typical anodization process.

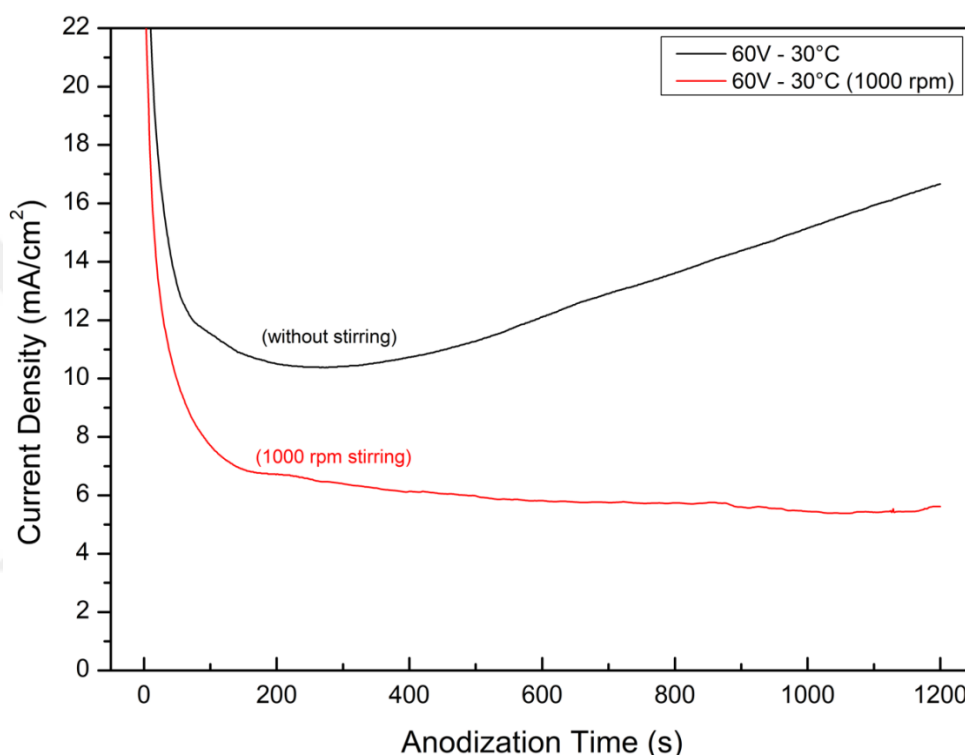


Figure 4.12 : Current density - time transient of samples anodized with (1000 rpm) and without stirring the electrolyte at 60 V and 30 °C for 20 min.

The FESEM images of the samples anodized at 60 V and 30 °C for 20 min without stirring and with 1000 rpm stirring conditions are compared in Figure 4.13. As can be seen from the images at the same magnification, the density and progression of the nanograss layer on the surface are much lower in the 1000 rpm stirred anodization condition (Figure 4.13(b)). This finding demonstrates that under severe conditions (high voltage and temperature), stirring stabilizes the anodization process and prevents heating up that may disrupt the regular morphology. Keeping the temperature under control prevents the formed anodic oxide from entering extreme chemical dissolution conditions and promotes more controlled anodization.

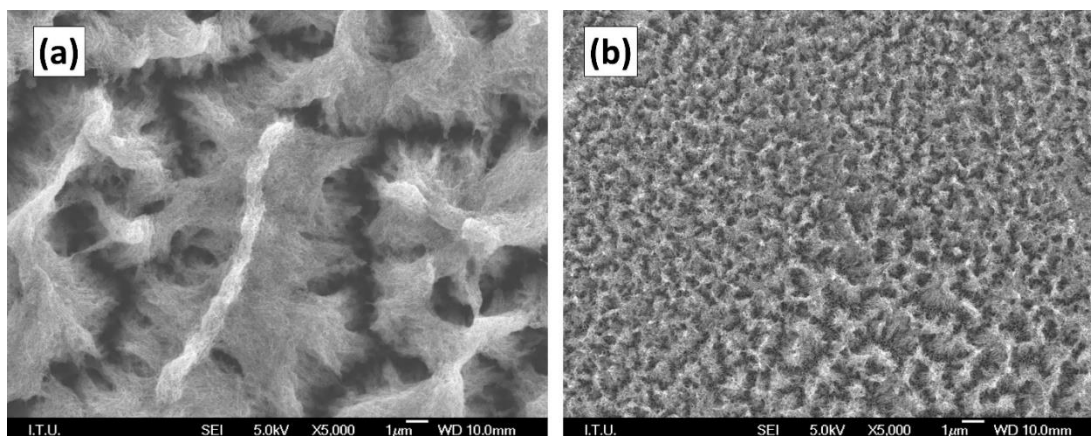


Figure 4.13 : FESEM images showing the morphology of the samples anodized at 60 V and 30 °C for 20 min: (a) without stirring, (b) with 1000 rpm stirring.

After confirming the contribution of stirring to temperature control and observing its significant effect on morphology, a series of experiments was conducted to observe the effects of different stirring rates. The anodization condition was kept constant as the non-stirred experiments to make accurate comparisons. Anodization experiments were performed at stirring rates of 250 rpm, 500 rpm, 750 rpm, and 1000 rpm at 50 V and 30 °C for 20 min. In Figure 4.14, the time-dependent current densities at different stirring rates are graphically presented. An apparent decrease is seen in current densities with the increase of stirring rate (Figure 4.14), which is consistent with the literature. Although there is no significant difference in current density between the non-stirred and 250 rpm stirred conditions, a significant decrease is observed at 500 rpm and higher stirring rates. In addition, it became possible to control anodization temperature with an accuracy of ± 0.1 degrees at a stirring rate of 500 rpm and above.

In several experiments, in which 1000 rpm stirring was utilized, it was observed that the magnetic bar lost its trajectory and rotational continuity at some point during the anodization. The current density data of 1000 rpm stirred condition in Figure 4.14 was chosen as one of the experiments in which the bar's rotational continuity was lost to show its effect on the process. It is seen that the current density increased immediately when the stirring continuity was lost. As the anodization electrolyte is an ethylene glycol-based solution, which is a viscous liquid, it was estimated that the stirring bar is forced out of its trajectory and lost its continuity above a specific stirring rate (1000 rpm and above). Besides, when the stirring rate was manually changed during anodization, increases and decreases in current density in response to change in the stirring rate were observed clearly.

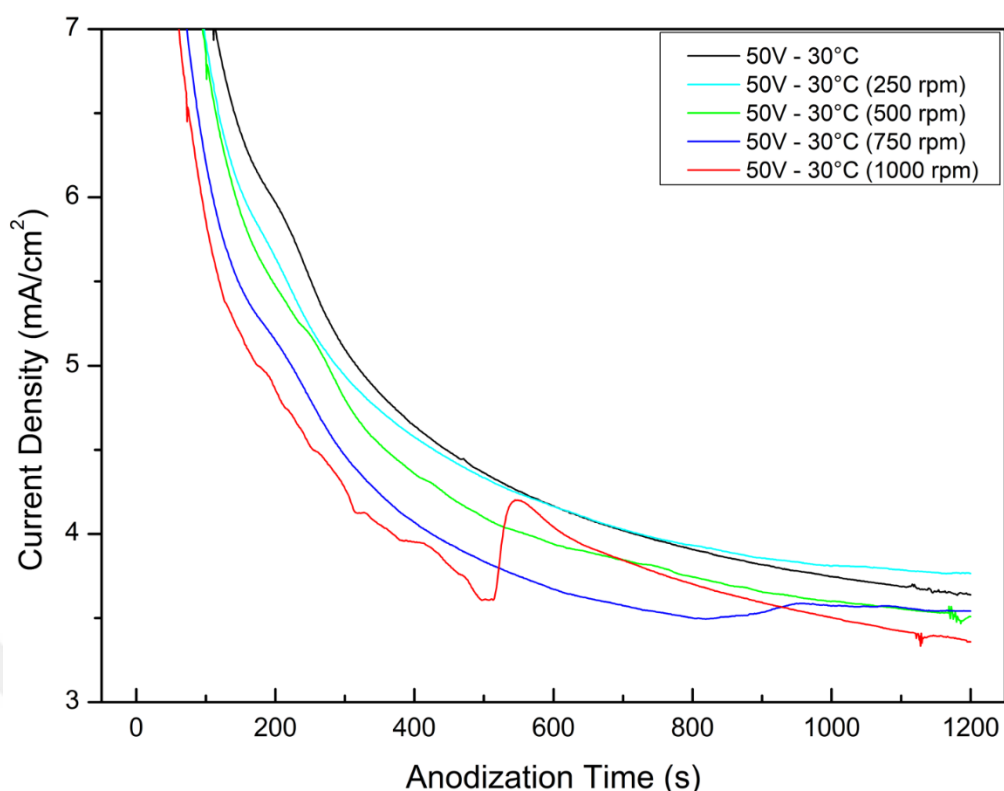


Figure 4.14 : Current density - time transient of samples anodized at 50 V and 30 °C for 20 min under different stirring rates (0 to 1000 rpm).

FESEM investigation of the anodization performed under different stirring rates was conducted to see the effects of stirring rate on the morphology. In the sample anodized without stirring, a barrier oxide layer that contains small gaps where nanotubes are apparent was monitored on the surface (Figure 4.10). When the stirring rate was set to 250 rpm, the gaps in the barrier oxide film enlarged slightly, increasing the total area in which the nanotubes were visible (Figure 4.15).

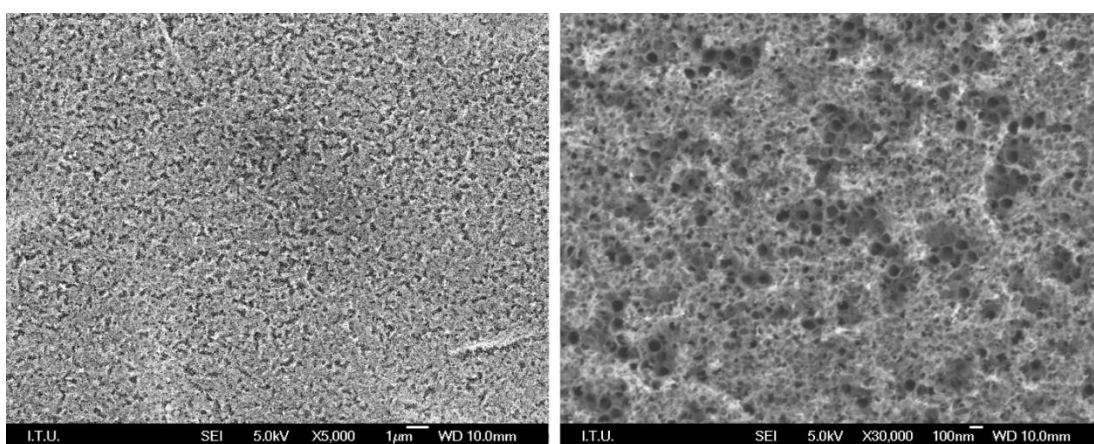


Figure 4.15 : FESEM images showing the morphology of the sample anodized at 50 V and 30 °C for 20 min under 250 rpm stirring.

When the stirring rate was increased to 500 rpm, it was seen that the barrier oxide film covering the surface turned into a relatively loose structure, and the open areas where open-top nanotubes were increased considerably (Figure 4.16).

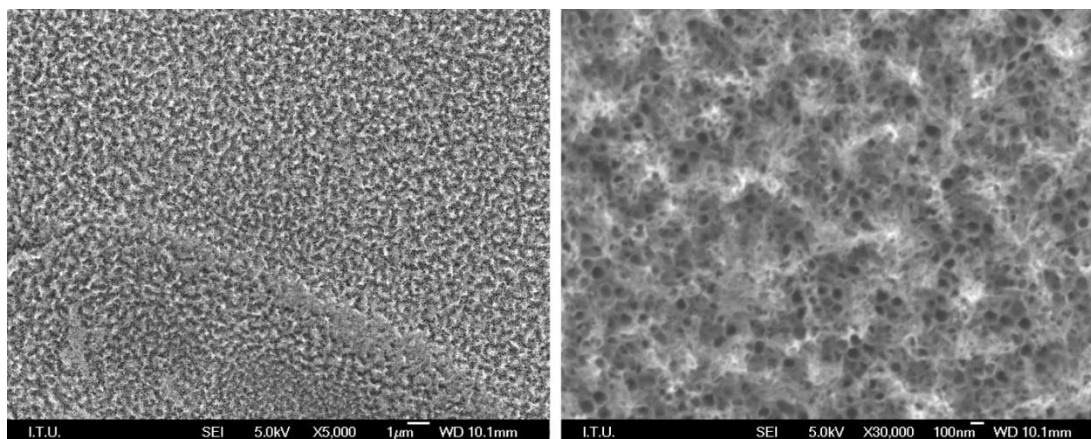


Figure 4.16 : FESEM images showing the morphology of the sample anodized at 50 V and 30 °C for 20 min under 500 rpm stirring.

In the anodization at 750 rpm stirring rate, the barrier oxide film covering the surface was virtually absent except for a small amount of residue. The sample was covered entirely with an open-top nanotube array (Figure 4.17).

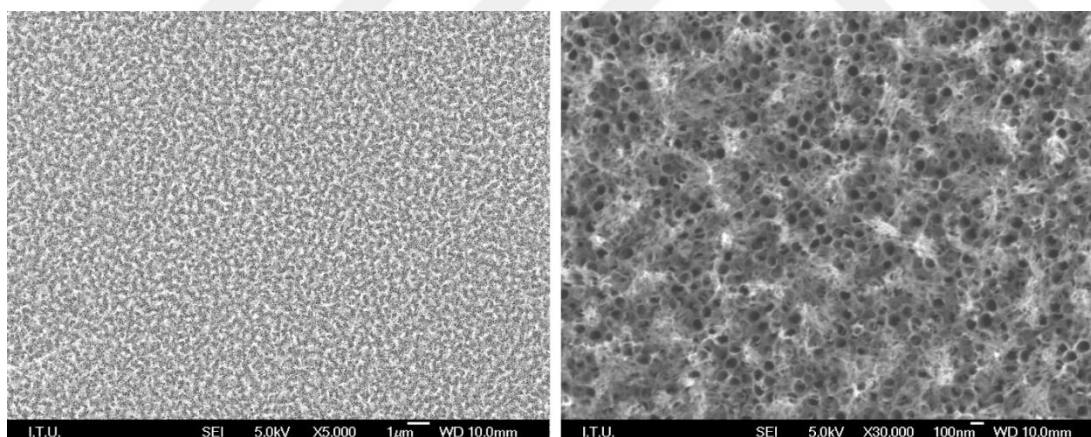


Figure 4.17 : FESEM images showing the morphology of the sample anodized at 50 V and 30 °C for 20 min under 750 rpm stirring.

In the anodization performed under 1000 rpm stirring, a morphology similar to the one obtained under 750 rpm stirring was obtained (Figure 4.18). Although a proper interpretation cannot be made due to the problems experienced during stirring, it is estimated that an even more clean surface structure would be obtained under 1000 rpm stirring if the stirring continuity could be ensured during the anodization experiment.

The anodization studies carried out under different stirring rates demonstrated that the stirring rate has a strong effect on the morphology. The barrier oxide film on the top surface disintegrates faster with an increasing stirring rate. We interpret this situation as an increased chemical dissolution rate on the barrier film with increased stirring speed. The chemical dissolution process of the barrier oxide film will be investigated in detail in the following sections.

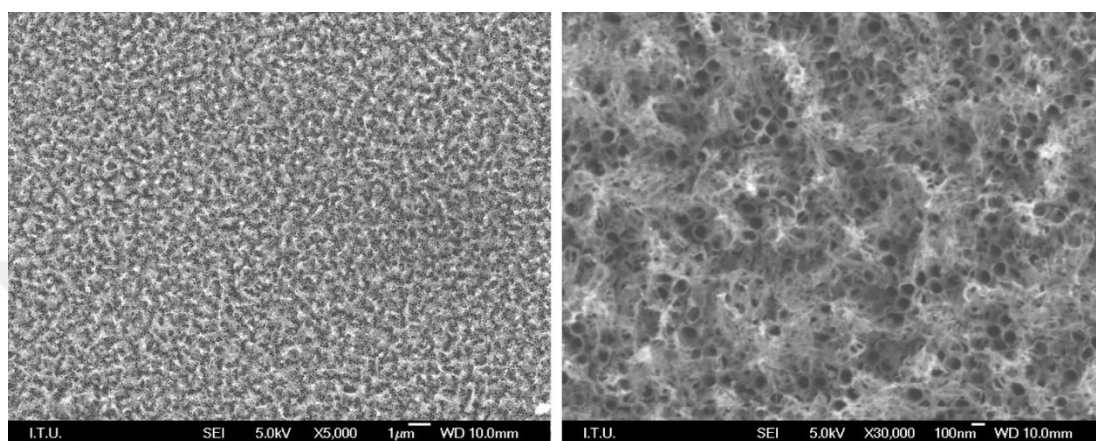


Figure 4.18 : FESEM images showing the morphology of the sample anodized at 50 V and 30 °C for 20 min under 1000 rpm stirring.

In addition, the positive effect of high stirring rate on the temperature control during anodization was clearly observed. Even though in the anodization performed under 1000 rpm stirring did not provide proper stirring continuity, all anodization experiments conducted at 750 rpm and lower stirring rates were able to be completed without any problems. Thus, in the experiments, it was decided to use 750 rpm stirring rate, which was found to be a stable parameter that provides effective temperature control and reproducible anodization conditions. Optimized stirring rate (750 rpm by using a 2 cm magnetic bar) was used in the following experiments in this section and in the formation and growth kinetics studies.

4.1.3 Effects of reuse of the anodization electrolyte

It is known that ethylene glycol-based anodization electrolytes absorb a significant amount of moisture when stored in atmospheric conditions due to their high affinity for water [91]. Also, the amount of water in the electrolyte has a significant effect on the conductivity of the solution and strongly affects the anodization process [68]. Therefore, the immediate use of fresh electrolytes is preferred to limit moisture absorption in anodization experiments conducted under atmospheric conditions. In this

study, the experimental studies were carried out in a glovebox with a controlled atmosphere; thus, moisture absorption of the anodization electrolyte while stored or during anodization was prevented.

Another crucial component of ethylene glycol-based anodization electrolyte is the fluoride ions. The anodic titanium oxide formed during the anodization combines with the fluoride ions in the solution and transforms into $[\text{TiF}_6]^{2-}$ and be solvated [18]. Thus, the amount of free fluoride ions in the electrolyte gradually decreases during the process. An anodization electrolyte prepared and used for a certain period is defined as an aged electrolyte. Aged electrolyte anodization is accomplished by using the electrolyte in preliminary anodization and then performing the main anodization. On the other hand, reusing the same electrolyte consecutively also results in the aging of the electrolyte. With each repeated use, the electrolyte becomes more aged, the amount of free fluoride in the solution decreases, and the anodizing properties of the electrolyte change. Especially if the anodization is not carried out under a controlled atmosphere (moisture-free), the water content of the electrolyte also changes, and as a result, anodization behaviors may change unpredictably. In the previous studies, it is seen that most of the studies on aging and re-utilization have been carried out under atmospheric conditions. For this reason, experimentally validating the literature data is needed.

Besides, in the literature, a decrease in the current density and growth rate due to the decreased fluoride ions have been demonstrated in several studies conducted on the anodization in the aged electrolytes and repeated use of the anodization electrolyte [81,82,86]. On the contrary, in some studies, it has been reported that current densities increase in anodization in the aged electrolytes due to the thicker barrier layer formed at the nanotube base [83,84]. Conflicting scientific reports provided another reason for the experimental investigation of aging behavior and reuse of anodization electrolytes.

In addition, literature studies have been focused on the effects of aging or reuse on growth and mechanical properties, but their effects on morphology have not been adequately studied. In this part, where the ideal condition of the electrolyte was sought, we focused on investigating and understanding the effects of aging and reuse of the electrolyte on anodization current density and final morphology.

Firstly, a fresh anodization electrolyte was prepared (0.6 wt % NH_4F , 1 vol % H_2O , EG), and four subsequent anodization experiments were performed at 50 V and 30 °C under 750 rpm stirring on the same day, in order to investigate the effect of repeated usage of the electrolyte on current density. It is seen in Figure 4.19 that the current density values visibly decrease in each repetition of subsequent anodization.

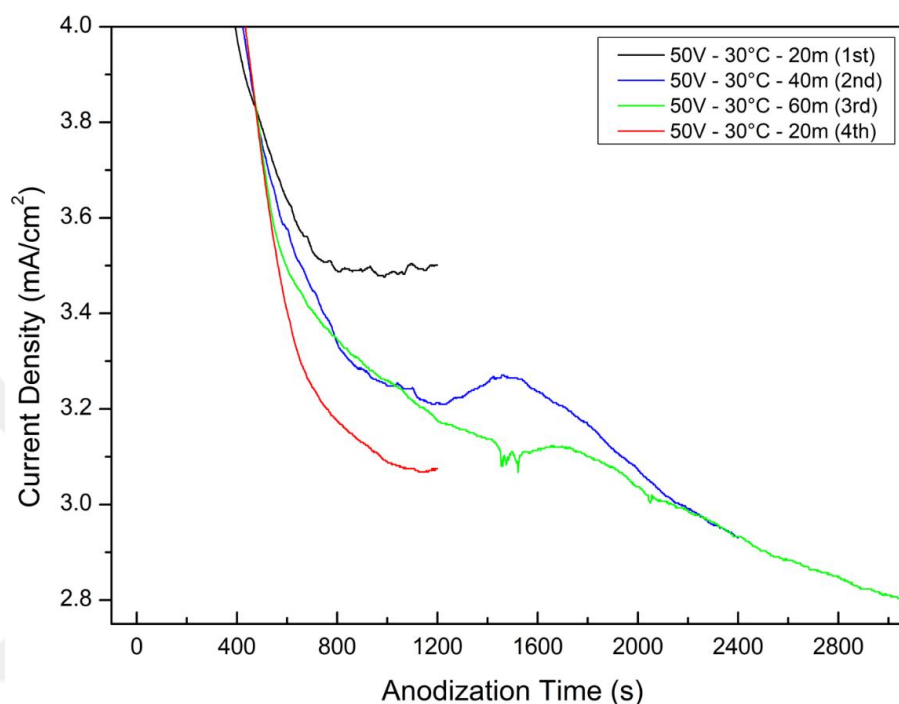


Figure 4.19 : Current density - time transient of samples repeatedly anodized on the same day at 50 V and 30 °C under 750 rpm stirring.

The 1st anodization and the 4th anodization of the same day are identical; however, the 1st anodization was carried out in a fresh electrolyte, while the 4th one was conducted using the same electrolyte (aged). When these two anodization experiments are compared (1st and 4th), it is seen that the current density has decreased significantly as the electrolyte is reused and aged (Figure 4.19). This decline in current density can be explained by the decrease in free fluoride ions in the electrolyte due to repeated anodization, which is consistent with the literature. The 2nd and 3rd anodization experiments were carried out for extended periods to clarify the aging effect on current density and morphology. The current density graphs of the 2nd and 3rd anodization samples confirm that the current density decreases as the electrolyte usage duration increases.

Significant findings were obtained in the morphological examinations of the 1st and 4th samples, which were anodized under identical conditions (at 50 V and 30 °C for 20

min under 750 rpm stirring). It was known from the previous experiments that the anodization using these parameters leads to an open-top nanotube array and thus is used as a reference. In Figure 4.20, surface and tilted FESEM images of structures formed using equivalent anodization parameters in fresh (1st sample) and aged (4th sample) electrolytes are given.

Open-top nanotubes under some residue are seen on the surface of 1st sample, which was anodized in the fresh electrolyte (Figure 4.20(a)). On the other hand, a compact barrier oxide layer completely covers the surface, and no nanotubes are visible in the 4th sample, which was anodized in the aged electrolyte (Figure 4.20(b)). In the tilted image of the 1st sample, one of two possibilities is seen as the rough residual structure on the surface: i) the residues of the barrier oxide layer after dissolution ii) the early phase of nanograss formation (Figure 4.20(c)). Instead, as can be seen in Figure 4.20(d), a flat barrier oxide layer exists on the surface of the 4th sample, as the chemical dissolution of the layer has not yet reached the level that will disrupt the integrity of the layer (Figure 4.20(d)). This difference was attributed to the prolongation of the time required for the barrier oxide layer dissolution because of the reduction in free fluoride in the aged electrolytes.

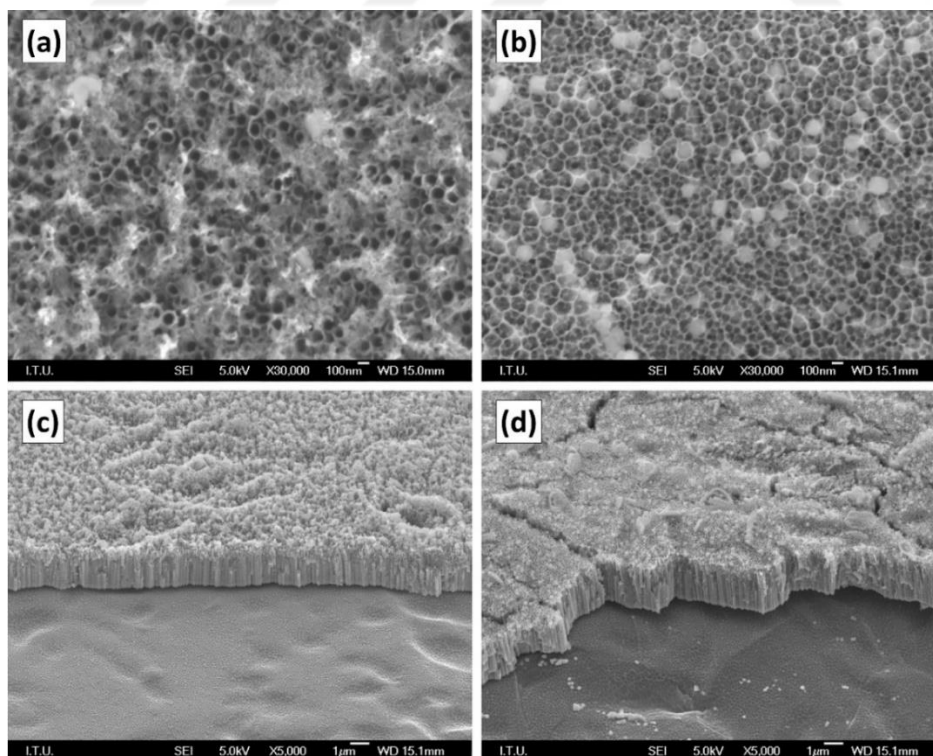


Figure 4.20 : FESEM images showing the morphology of the sample anodized at 50 V and 30 °C for 20 min under 750 rpm stirring in (a), (c) fresh; and (b), (d) aged anodization electrolyte.

Three identical anodization experiments were carried out to investigate the effect of aging and reuse of the electrolyte at different anodization temperatures. Experiments were conducted sequentially on the same day at 50 V and 15 °C for 30 min under 750 rpm, starting with a fresh electrolyte. As shown in Figure 4.21, while current density levels are relatively lower than the anodization conducted at 30 °C due to the lower reaction rates because of the lower temperature, the downshifting effect of aged electrolyte on current density is confirmed again at 15 °C. The current density shift is not visible in the first 5 minutes of anodization due to the steep descent in the current, but after 5 minutes, the current density value strongly shifts down depending on the repetition of use.

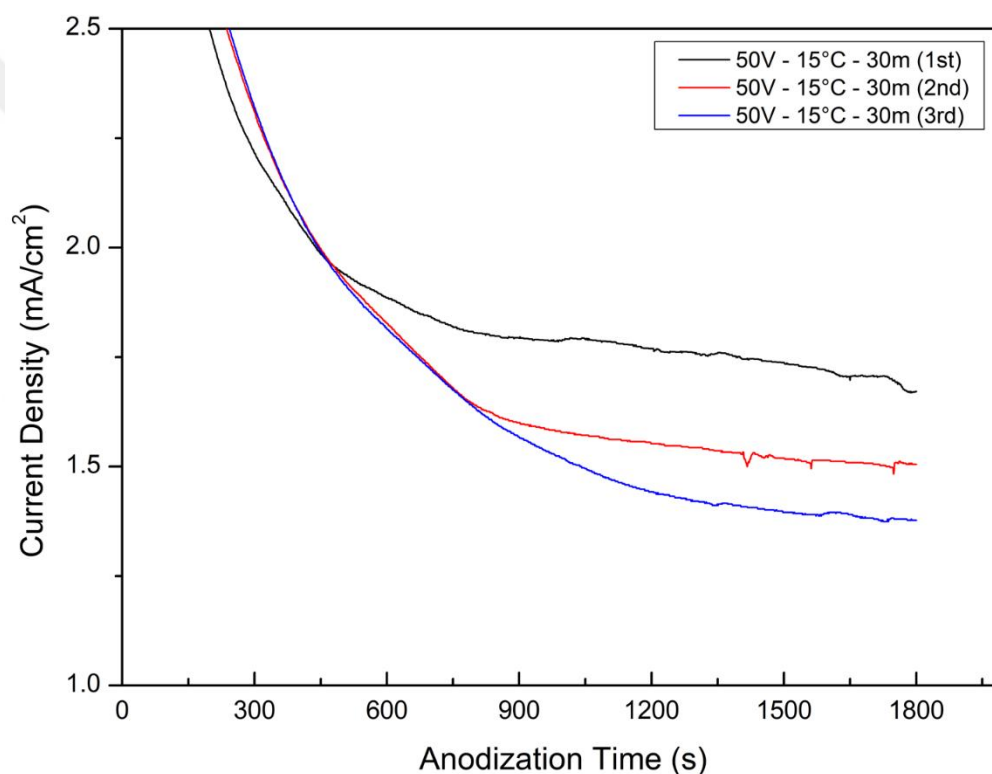


Figure 4.21 : Current density - time transient of samples anodized repeatedly on the same day at 50 V and 15 °C for 30 min under 750 rpm stirring.

FESEM images of sequentially anodized samples at 50 V and 15 °C for 30 minutes under 750 rpm stirring are given in Figure 4.22. The surface was completely covered with a barrier layer for all three samples, and the nanotubes were not visible. However, when tilted FESEM images are examined, it can be seen that the nanotubes are present under this layer. Besides, when the morphology of the surface barrier layers was examined, it was observed that the integrity of the barrier layer on the 1st sample (anodized in the fresh electrolyte) was more distorted than the 2nd and 3rd sample,

which can be interpreted as the dissolution process of the barrier layer on the 1st sample is at a more progressed state compared to other samples (Figure 4.22(a)). It was observed that the firmness of the barrier oxide layer was slightly higher in the 2nd sample (Figure 4.22(b)). In the 3rd sample, the firmness of the layer was the highest compared to the other samples (Figure 4.22(c)). This observation also supports that the chemical dissolving power of the electrolyte on the surface barrier oxide film decreases as the electrolyte is reused and aged.

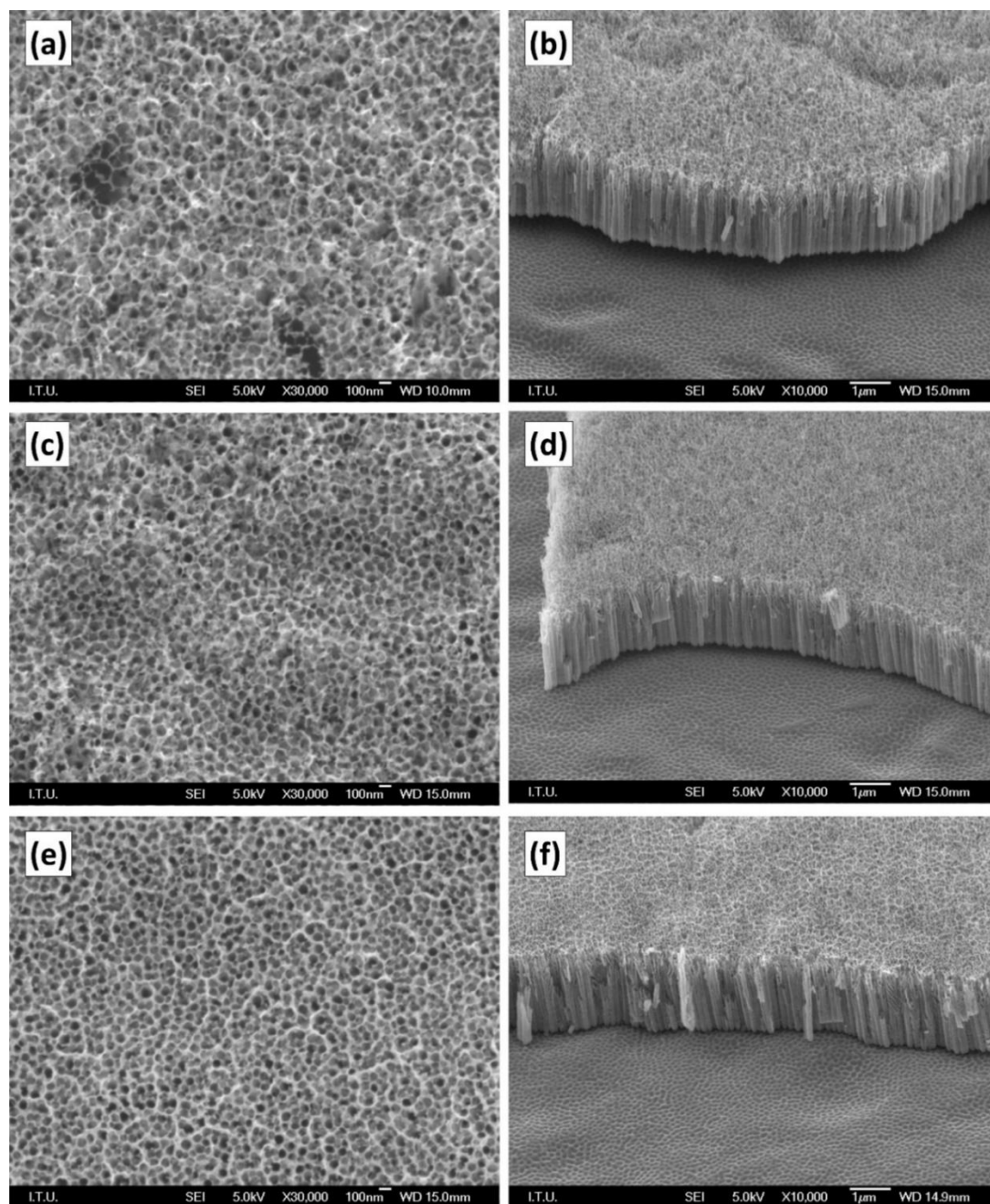


Figure 4.22 : FESEM images showing the morphology of the sample anodized consecutively in the same electrolyte at 50 V and 15 °C for 20 min under 750 rpm stirring: (a), (b) 1st anodization; (c), (d) 2nd anodization; (e), (f) 3rd anodization.

In order to observe the aging and re-utilization effects more systematically, an experiment plan was prepared that includes anodization experiments to be performed on different days and in different aged electrolytes. All experiments were performed in the same electrolyte, starting with a fresh solution according to the plan. As the details are given in Table 4.1, comparison samples were anodized on the 1st, 3rd, and 5th day at 50 V and 20 °C for 60 min under 750 rpm stirring; and dummy samples, which were only employed to age the electrolyte, was anodized on the 2nd and 4th day at 50 V and 20 °C for 180 min under 750 rpm stirring. The electrolyte was aged by performing two dummy on the 2nd day and three dummy anodization experiments on the 4th day. In order to observe the effects of repeated use in more detail, the electrical charge passing through the system was recorded during the experiments.

Table 4.1 : Experimental data of the samples anodized using the same anodization electrolyte on different days at 50V and 20 °C for 60 min under 750 rpm stirring.

Experiment Day	Sample Type	Anodization condition	Charge consumed during anodization (C)	Cumulative charge passed through the electrolyte (C)
Day 1	Sample 1	50V – 20 °C – 60 min	35.58	35.58
Day 2	Dummy plate	50V – 20 °C – 180 min (2x)	192.37	227.95
Day 3	Sample 2	50V – 20 °C – 60 min	33.84	261.79
Day 4	Dummy plate	50V – 20 °C – 180 min (3x)	265.10	526.89
Day 5	Sample 3	50V – 20 °C – 60 min	31.67	558.56

In the time-dependent current density graphs of three comparison samples (Figure 4.23), it can be seen that the current density values of the anodization performed in aged solutions shifted down, as expected. Along with the downward shift of the current density, the amount of electrical charge consumed in equivalent anodization also decreases. Although the samples with the identical surface area were anodized under the same conditions and for the same duration, the electrical charge of 35.58 C in

Sample 1, the electrical charge of 33.84 C in Sample 2, and the electrical charge of 31.67 C in Sample 3 were consumed during anodization.

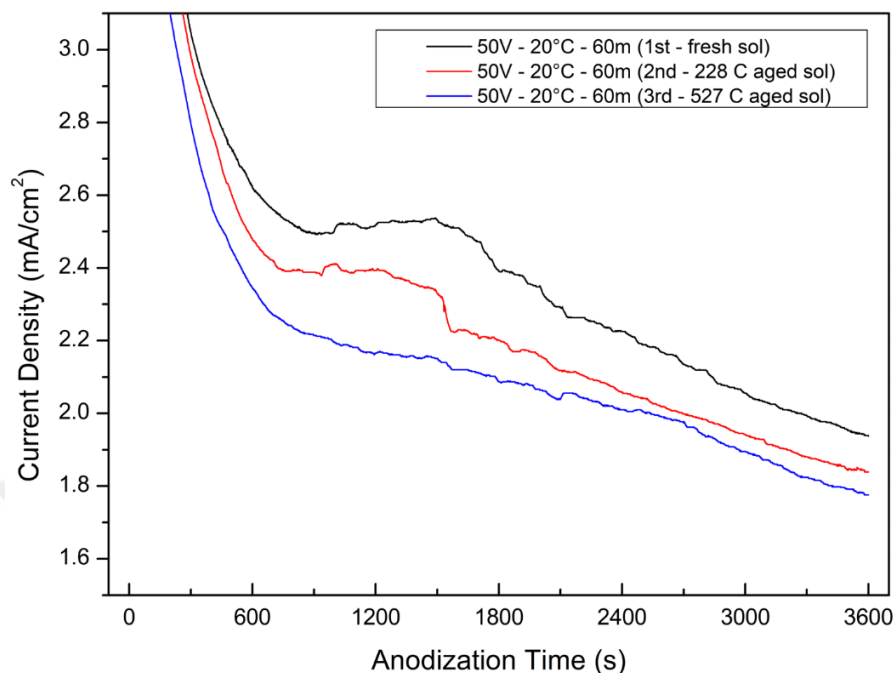


Figure 4.23 : Current density - time transient of samples anodized using the same anodization electrolyte on different days at 50 V and 20 °C for 60 min under 750 rpm stirring.

During the two dummy anodization experiments performed on the 2nd day, 192.37 C electrical charge passed through the system, and in response to this, a 4.9 % decrease in electrical charge consumption was observed between the sample anodization performed before (Sample 1) and after (Sample 2) dummy anodization. Moreover, in the three dummy anodization experiments performed on the 4th day, an electrical charge of 265.10 C passed through the system this time. In response, a 6.4 % decrease in electrical charge reduction was observed between the sample anodization performed before (Sample 2) and after (Sample 3) this dummy anodization. It was determined that there was a proportional correlation between the reduction rates in the electrical charge consumed during the comparison of sample anodization and the amount of electrical charge passing through the system during electrolyte aging using dummy samples.

It is known that the amount of charge passing through the system during anodization is directly proportional to the amount of anodized titanium [26]. From this point of view, the amount of electrical charge consumed during anodization can represent the amount of fluoride consumed in the electrolyte. Although the aging state of the

electrolyte is usually defined in terms of usage duration in the literature, defining the electrolyte aging in terms of electrical charge consumed during the aging anodization can provide more accurate results.

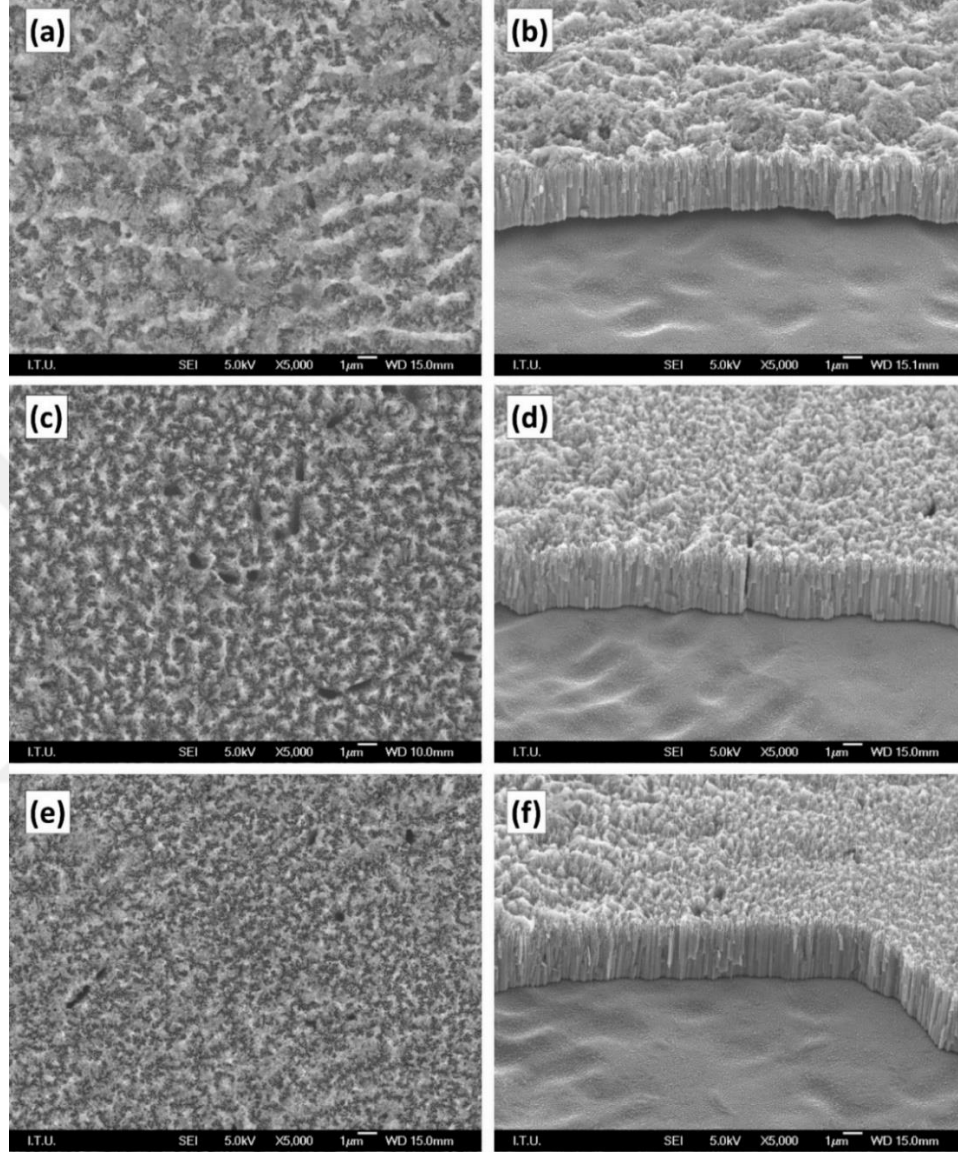


Figure 4.24 : FESEM images showing the morphology of the samples anodized using the same anodization electrolyte on different days at 50 V and 20 °C for 60 min under 750 rpm stirring: (a),(b) in a fresh electrolyte (Sample 1); (c),(d) in 227.95 C aged electrolyte (Sample 2); (e),(f) in 526.89 C aged electrolyte (Sample 3).

When the anodized samples produced in different aged electrolytes were examined morphologically, significant information was obtained about a different phase of the chemical dissolution process. A dense nanoglass structure consisting of large bundles was observed on the surface of Sample 1, which was anodized in the freshly prepared electrolyte (Figure 4.24(a) and (b)). However, in the case of anodization in 228 coulombs aged electrolyte (Sample 2), bundles of the nanoglass layer were smaller in

size, and the overall structure was less dense compared to Sample 1 (Figure 4.24(c) and (d)). Furthermore, it was observed that the nanoglass layer formed on Sample 3, which was anodized using 527 coulombs aged electrolyte, had the tiniest nanoglass bundles and thinner structure that gives the impression that it was in the early formation phase (Figure 4.24(e) and (f)).

The effect of electrolyte aging on the chemical dissolving power of the electrolyte was previously observed on the barrier oxide layer. This effect, which significantly influences the chemical dissolution process, was also observed in this set of experiments on the nanoglass structure. It is known that nanoglass structures are formed due to chemical dissolution, especially during long anodization [29]. In the anodization experiments conducted in fresh and aged electrolytes under the same anodization conditions, it was determined that the chemical dissolving power of the electrolyte changed remarkably depending on the aging of the electrolyte, which was attributed to the reduced amount of free fluoride ions in the solution.

Subsequently, two additional anodization experiments were added to the experimental plan to investigate the effect of repeated usage in the aged electrolyte. Another anodization (2nd anodization of the day) was performed on the 5th day using the 527 coulombs aged electrolyte. Then, final anodization was performed with the same electrolyte on the 6th day using the same parameters again.

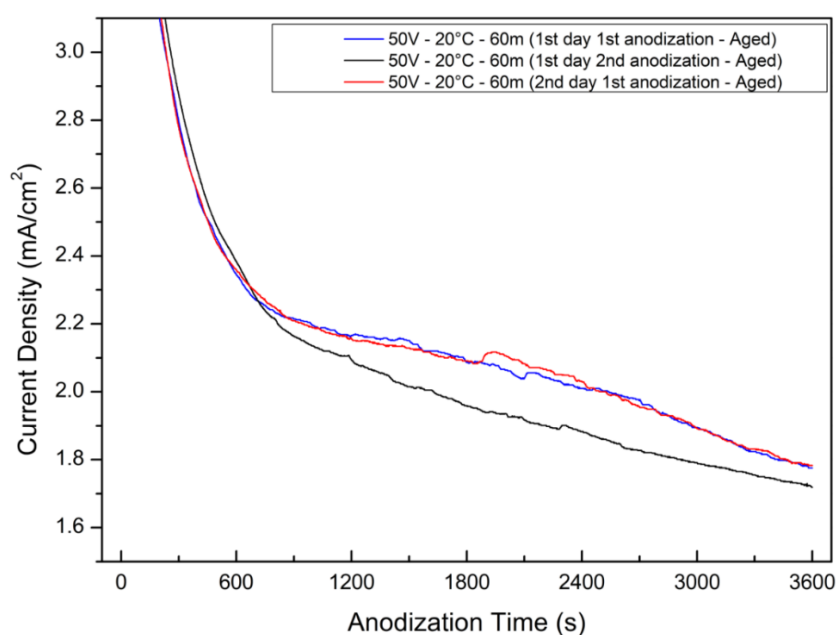


Figure 4.25 : Current density - time transient of samples sequentially anodized using 527 C aged anodization electrolyte at 50 V and 20 °C for 60 min under 750 rpm stirring.

As a result, a remarkable finding was observed that was not reported in the literature before. As shown in Figure 4.25, the current density plot of the 2nd anodization of the day shifted downwards compared to the 1st anodization of the day, consistent with the earlier experiments. However, in the anodization performed the next day, after the electrolyte rested overnight (inside the glovebox), the current density values returned to similar levels (or slightly below) as the first anodization of the previous day.

In Figure 4.26, the current density data of all samples are presented, combining the data of Figure 4.23 and Figure 4.25. In the graph, downward shift in the current density because of the long-term aging of the electrolyte; a downward shift in the current density due to repeated anodization on the same day; and recovery in the current density (shifting back up) with anodization performed in the overnight rested electrolyte are seen together (Figure 4.26).

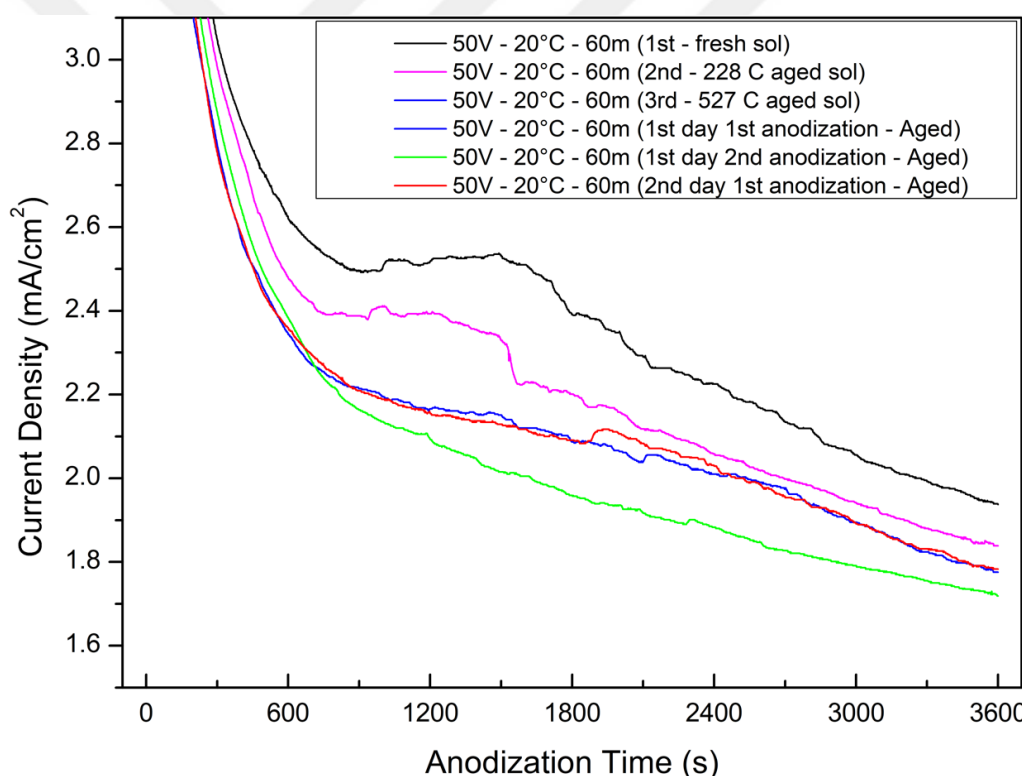


Figure 4.26 : Current density - time transient of samples anodized using the same anodization electrolyte on different days at 50 V and 20 °C for 60 min under 750 rpm stirring.

Surprisingly, the current density reduction observed in successive anodization performed on the same day was at a level similar to that observed in anodization performed in fresh and considerably aged electrolytes. In fact, in this section's first set of experiments, performing anodization on the same day significantly reduced the

current density; a decrease of ~12% was observed between the 1st and 4th anodization of the day (Figure 4.19). However, in the evaluation of the graph, the amount of decrease in current density has not been emphasized since the anodization experiments in highly aged electrolytes and overnight rested electrolytes have not yet been specified in that section.

It is well-known that anodic titanium oxide and titanium ions that diffuse through the formed oxide during anodization combine with free fluoride ions in the electrolyte to form water-soluble $[\text{TiF}_6]^{2-}$ species and be solvated [18]. Therefore, the amount of $[\text{TiF}_6]^{2-}$ species in solution is expected to increase with the utilization of the electrolyte. With the extended use of the electrolyte, the transparent color of the electrolyte turned into a purple-like color. The increased duration of use further darkened the color of the electrolyte, indicating the increased concentration of the purple color-giving species. It can be seen in Figure 3.1 how the excessively aged electrolyte looks like in the plastic container, which turned purple and darkened after long-term use (fresh electrolytes on the shelf, over-aged electrolytes at the bottom). When the darkened solution was kept unused for some time, it was observed that a purple precipitate accumulated at the bottom of the plastic container. Since all the preparation and the anodization processes were carried out in the glovebox, the electrolyte was not contaminated with any external components.

On the other hand, it is known that the $[\text{TiF}_6]^{2-}$ species are not very stable and tend to decompose as titanium fluorides or oxyfluorides [92]. Among the fluorinated compounds of titanium that can precipitate in this solution (i.e., TiOF_2 , TiF_4 , TiF_3), the only purple-colored component is TiF_3 . During the formation of $[\text{TiF}_6]^{2-}$ species, six fluoride ions bind to each titanium atom, and the amount of free fluoride in the electrolyte is significantly reduced during anodization. We estimate that when the electrolyte is kept unused for a convenient duration after anodization, $[\text{TiF}_6]^{2-}$ species decompose into TiF_3 , releasing three fluorides (for each molecule); thus, the amount of free fluoride in the electrolyte increases again. Accordingly, when the anodization is performed again after the electrolyte recovered, the current density level returns to the level of the previous anodization.

We believe that conversion of $[\text{TiF}_6]^{2-}$ species into TiF_3 cannot occur due to insufficient recovery time in anodization experiments conducted consecutively on the same day. So, the current density values downshift because of the drastic decrease in

free fluoride in the electrolyte. When the electrolyte is kept unused for a sufficient time to enable conversion of $[\text{TiF}_6]^{2-}$ species into TiF_3 , the current density value increases again. It has been experimentally determined that an overnight resting of the electrolyte is sufficient for this recovery effect to be seen.

The experimental procedure was repeated at different temperatures to verify the current density shifts due to repeated use and electrolyte resting, test the recovery effect in a freshly prepared solution, and see if the recovery effect occurs at different temperatures. Anodization experiments were conducted, starting with a fresh electrolyte at 50 V and 15 °C for 30 min under 750 rpm stirring. 2 consecutive anodization were conducted on the same day, then the electrolyte was kept unused overnight, and then another anodization was carried out the next day.

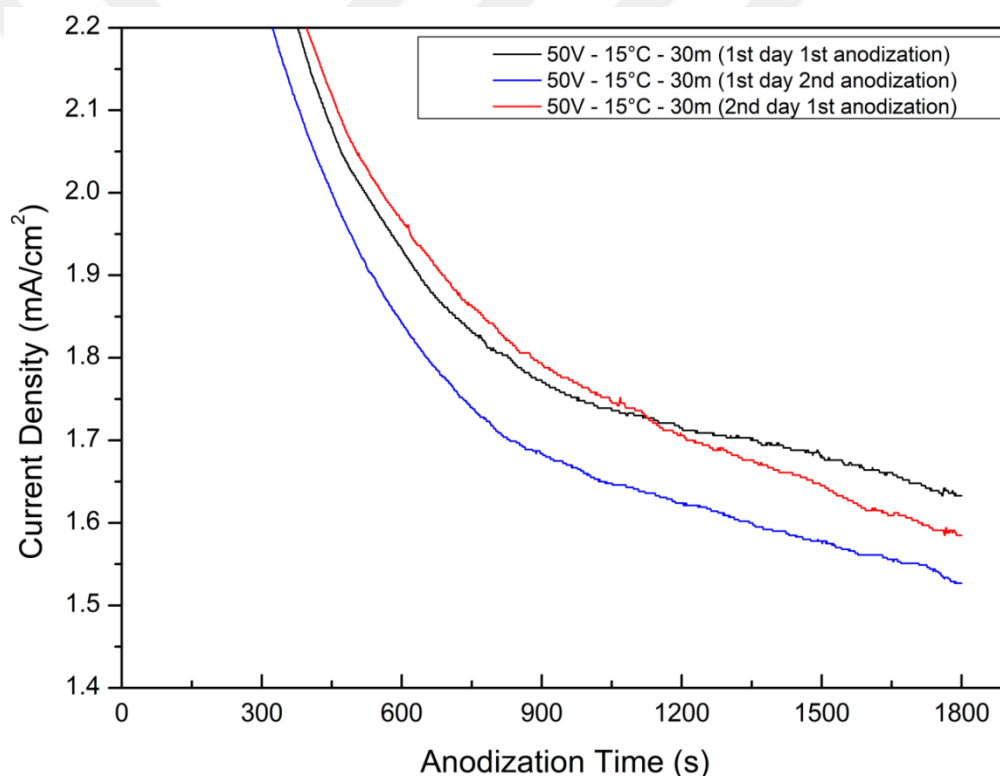


Figure 4.27 : Current density - time transient of samples sequentially anodized using a fresh anodization electrolyte at 50 V and 15 °C for 30 min under 750 rpm stirring.

As shown in Figure 4.27, a notable decrease was observed in the current density in the anodization performed on the same day. The current density returned to the initial anodization current density levels performed after overnight resting of the electrolyte. The recovery effect was confirmed again by experiments performed in a fresh electrolyte at 15 °C.

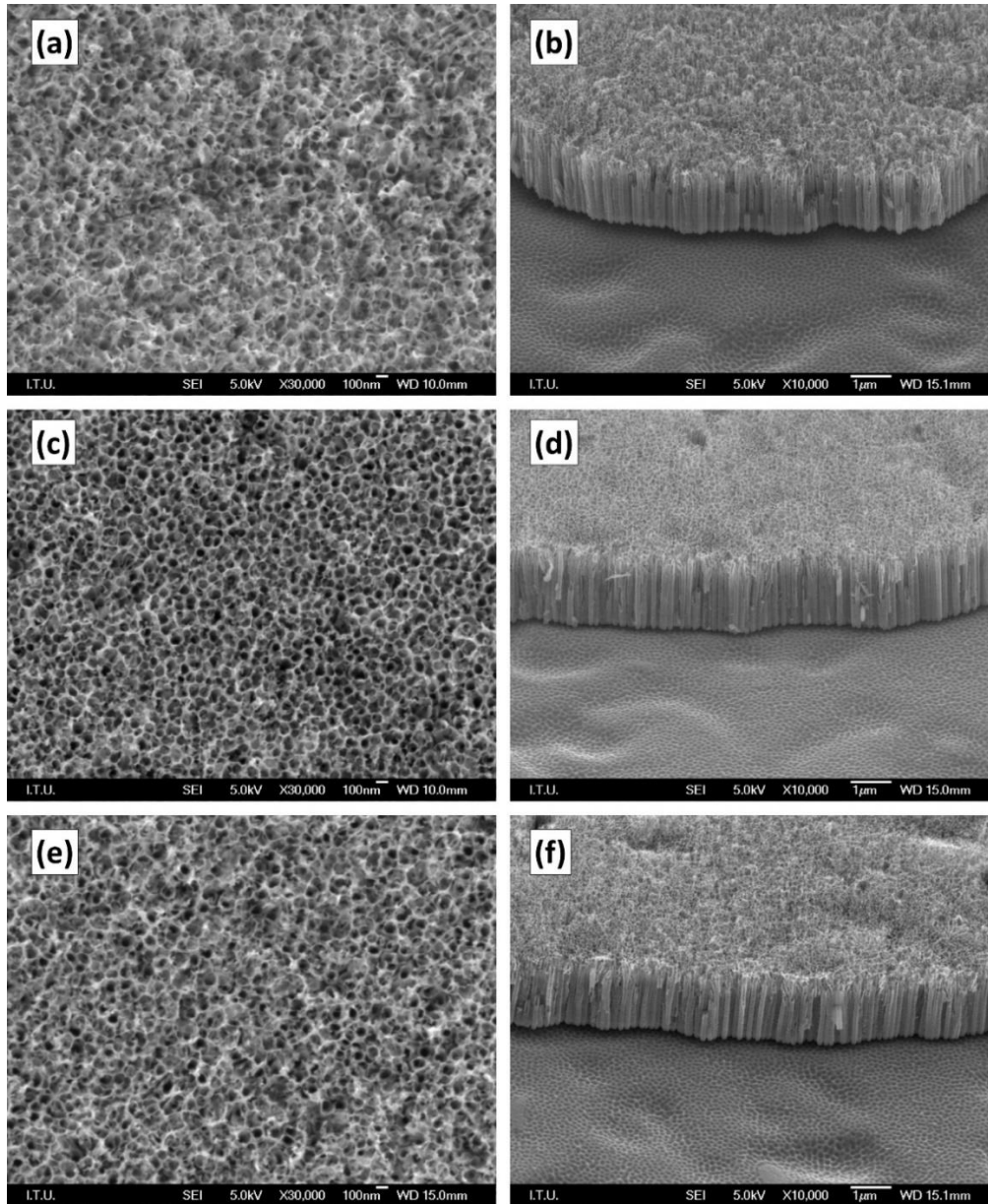


Figure 4.28 : FESEM images showing the morphology of the samples anodized sequentially using a fresh anodization electrolyte at 50 V and 15 °C for 30 min under 750 rpm stirring: (a), (b) 1st day 1st anodization; (c), (d) 1st day 2nd anodization; (e), (f) 2nd day 1st anodization.

FESEM images of the samples are presented in Figure 4.28. The sample's surface, which anodized in the fresh electrolyte, was covered with a barrier oxide film, but the film was in a stage where the layer's integrity was disrupted due to chemical dissolution. There were small gaps on the barrier oxide layer where nanotubes were slightly visible (Figure 4.28(a) and (b)). In the 2nd anodization of the same day, the surface was covered with a barrier oxide layer again, but the structure of the barrier film was compact without gaps (Figure 4.28(c) and (d)). The compact structure of the film indicates that the barrier oxide was exposed to less chemical degradation than the

1st sample. In other words, the chemical dissolving power of the electrolyte decreased as expected as a result of repeated use. In the anodization performed the next day after the overnight resting of the electrolyte, the morphology of the surface barrier film was very similar to the morphology of the barrier film obtained in the first anodization of the previous day (Figure 4.28(e) and (f)). As a result of the overnight resting, chemical dissolving power of the electrolyte also returns to a level close to the fresh electrolyte of the previous day.

The same experimental procedure was repeated by anodization at 50 V and 10 °C for 30 min under 750 rpm stirring, starting with a fresh electrolyte. As shown in Figure 4.29, while the current density level decreased in the subsequent anodization on the same day, as expected, it returned to fresh solution current density level after overnight resting of the electrolyte.

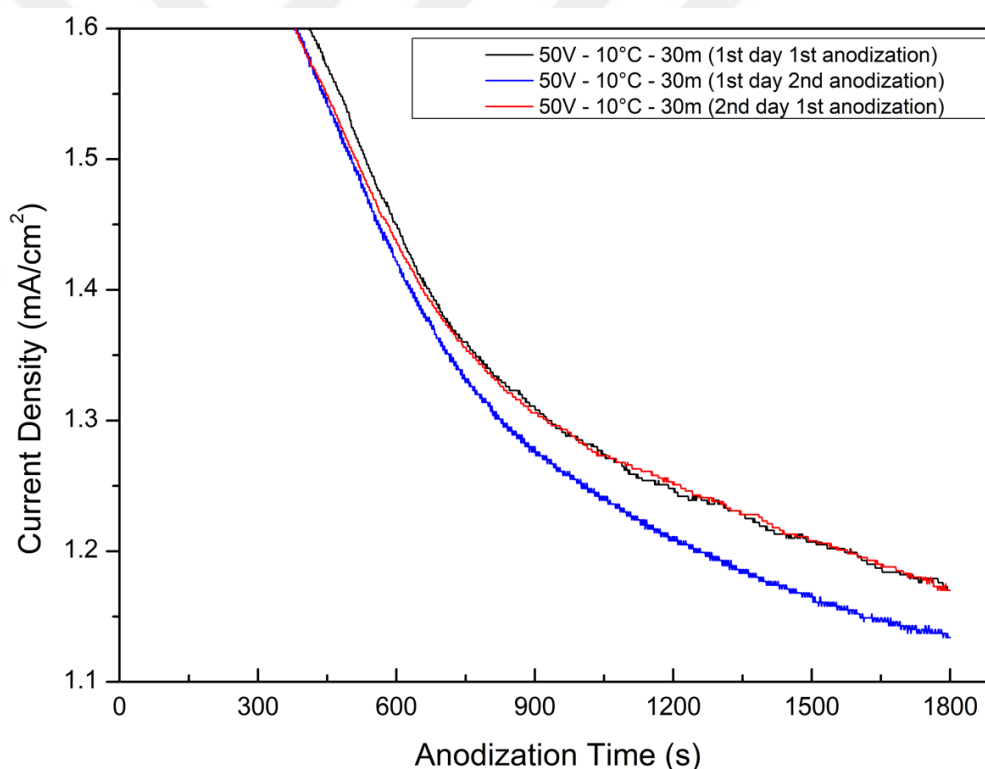


Figure 4.29 : Current density - time transient of samples sequentially anodized using a fresh anodization electrolyte at 50 V and 10 °C for 30 min under 750 rpm stirring.

In all experiments carried out at 10 °C, a compact barrier oxide layer is observed on the surface of the samples (Figure 4.30). As the anodization conditions (low temperature and short anodization duration) were not sufficient for the progression of chemical degradation in the top barrier oxide film, only slight differences could be seen between the sample morphologies, and no distinctive observation could be made.

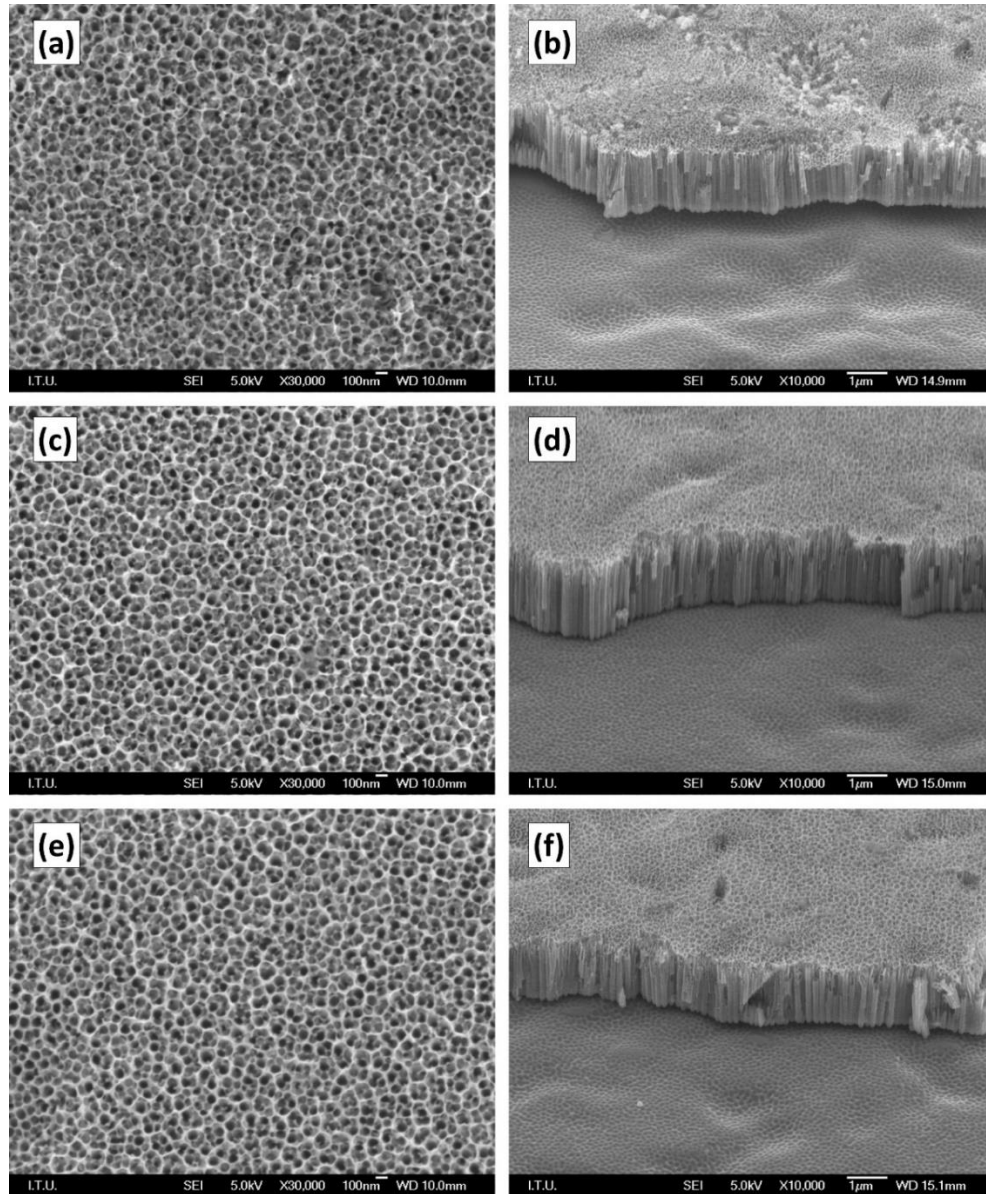


Figure 4.30 : FESEM images showing the morphology of the samples anodized sequentially using a fresh anodization electrolyte at 50 V and 10 °C for 30 min under 750 rpm stirring: (a), (b) 1st day 1st anodization; (c), (d) 1st day 2nd anodization; (e), (f) 2nd day 1st anodization.

As an additional finding, the current density values stabilized for a while and even increased during some anodization experiments (Figure 4.26). These unstable regions were observed during anodization at relatively high temperatures and in fresh electrolytes. It has been noticed that this current behavior coincides with the period when the barrier oxide is completely dissolved during anodization. The complete dissolution of the surface barrier oxide layer during anodization leaves the nanotubes open-topped. The clearance of the top layer on the nanotubes increases the surface area and results in a geometry where more current can flow through the system. When this process, which is based on the chemical dissolution, happens too quickly, unstable

regions of current density (stabilization or increase) are seen due to a sudden drop in the system resistance caused by surface area increase. Indeed, in anodization carried out at lower temperatures or in aged electrolytes, this irregular current density behavior either decreases or does not occur at all. The chemical dissolving power of the electrolyte decreases in anodization performed at low temperatures or in aged electrolytes; therefore, the complete dissolution of the barrier layer becomes a slower and time-consuming process. As the dissolution process of the barrier layer spreads over time, sudden surface increases are prevented, and thus, unstable regions in the current density do not occur. In the formation and growth kinetic studies, which will be explained in the following sections of this thesis, the electrolyte composition with a lower fluoride concentration was used to investigate the barrier oxide dissolution processes comfortably. The lower fluoride concentration causes the chemical dissolving power of the electrolyte to decrease, and the chemical dissolution proceeds more slowly. During these studies using lower fluoride content, unstable regions of current density (stabilization or increase) were not observed, supporting our estimation that these regions occur due to the rapid disappearance of the barrier layer.

As the last experiment of this part, a comparative anodization was performed in a 750 coulomb aged solution at 50 V and 30 °C for 20 min under 750 rpm stirring, as the first usage of the day.

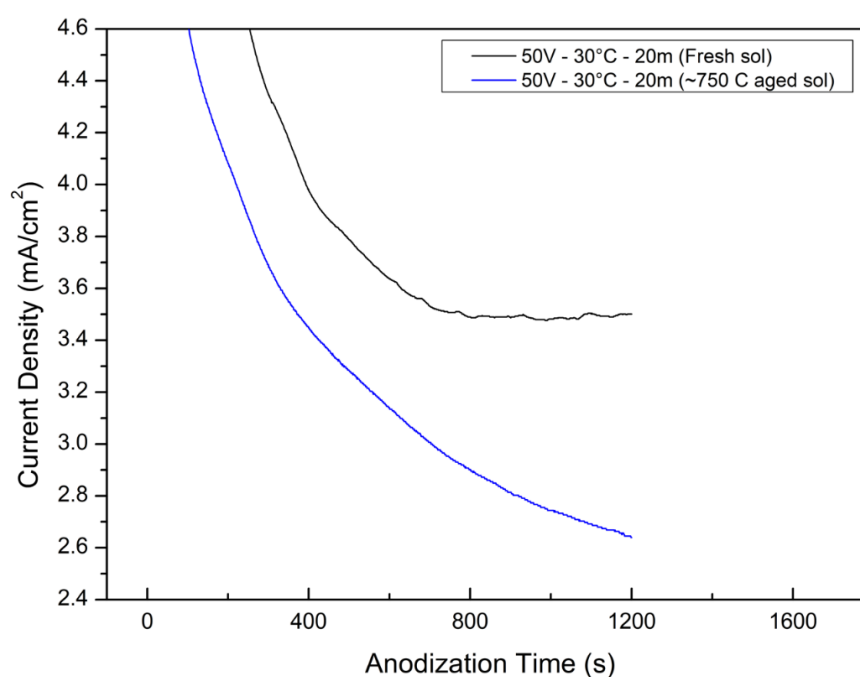


Figure 4.31 : Current density - time transient of samples anodized at 50 V and 30 °C for 20 min under 750 rpm stirring in a fresh and 750 C aged electrolyte.

As shown in Figure 4.31, there is a significant difference (downshifting) between the current density plots of the fresh and aged electrolyte, as expected. When the samples were examined in terms of morphology, open-top nanotubes were observed in the sample anodized in the fresh electrolyte (the barrier layer was dissolved entirely). In contrast, the sample surface was completely covered with a barrier layer in the anodization performed in the aged electrolyte (Figure 4.32). The aging difference between the electrolytes may result in similar morphologies with different levels of chemical degradation, as often encountered in this section. However, when the aging difference between the electrolytes is too much, two completely different morphologies can be observed as in this example.

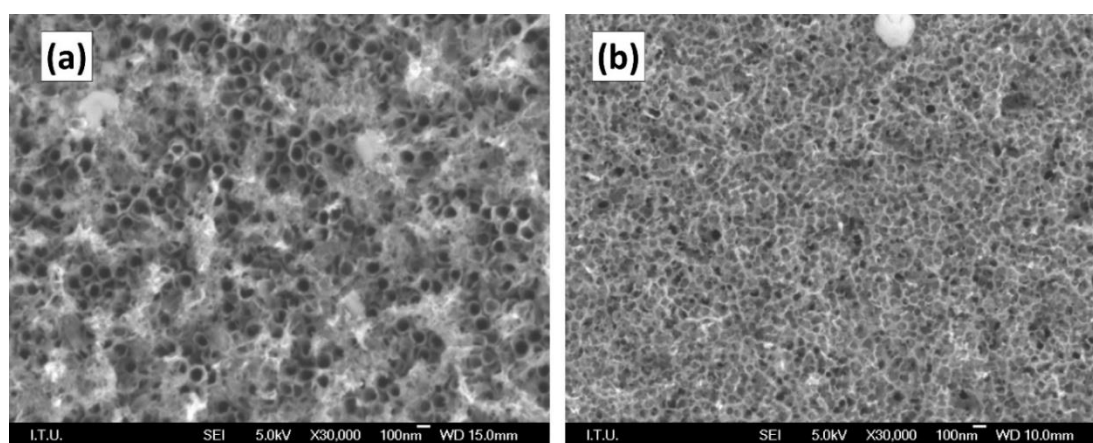


Figure 4.32 : FESEM images showing the morphology of the sample anodized at 50 V and 30 °C for 20 min under 750 rpm stirring in (a) fresh and (b) 750 C aged anodization electrolyte.

In conclusion, experimental studies on the aging and reuse of the anodization electrolyte have shown that current density behavior and morphology can vary significantly depending on the condition of the electrolyte. The reactions consume fluoride during anodization, and the amount of free fluoride in the electrolyte gradually decreases. It has been experimentally verified that the current density values shift down, and the chemical dissolving power of the electrolyte decrease in anodization conducted after prolonged usage or short but repetitive usage of the anodization electrolyte. However, it has been shown that when the electrolyte is kept unused overnight after anodization, almost equivalent current density values and morphological results can be obtained as the anodization of the previous day. It seems possible to obtain near-ideal results by performing one anodization per day and keeping the electrolyte overnight in an experiment plan that includes relatively short

anodization experiments that does not consume much electrical charge. On the other hand, equivalent results can always be obtained in anodization carried out in the glovebox using freshly prepared solutions. For this reason, in the formation and growth kinetic studies detailed in the following sections, it was decided to perform each anodization in a freshly prepared electrolyte inside a glovebox.

4.1.4 Effects of anodization voltage and temperature

Anodization potential is one of the most studied major anodization parameters and significantly affects current density, growth rate, and tube diameters. As the anodization potential increases, the anodization current density rises, and thus, the growth rate of the nanotubes increases [70,71]. In addition, it is known that nanotube diameters vary in direct proportion with the anodization potential [66]. However, the effect of the anodization potential on morphology has not been studied in detail. A basic experiment plan was prepared to observe the effect of anodization potential on morphology. We knew from the former experiments that an anodization conducted at 50 V and 30 °C for 20 min under 750 rpm stirring results in complete dissolution of the barrier oxide film, leaving an open-top nanotube structure on the surface. Therefore, taking this parameter as a reference, the voltage range of 45 V to 60 V was investigated to observe the voltage effect on the morphology.

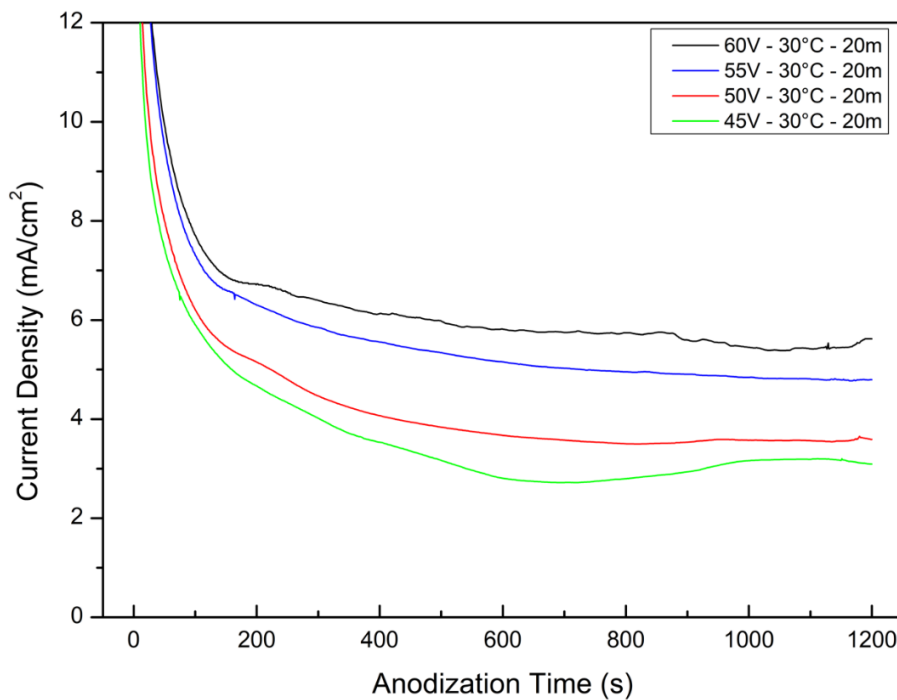


Figure 4.33 : Current density - time transient of samples anodized applying different potentials (45 V to 60V) at 30 °C for 20 min under 750 rpm stirring.

The change in current density during anodization is seen in Figure 4.33. Current density was expectedly lower for lower voltage and increased to higher as the potential was increased. No inconsistency is observed in the current density–time plots.

When the structures obtained as the result of anodization were examined morphologically, it was observed that the surface morphology showed slight changes depending on the potential. Surface FESEM images are presented at different magnifications (30.000x and 5.000x) in Figure 4.34 and Figure 4.35.

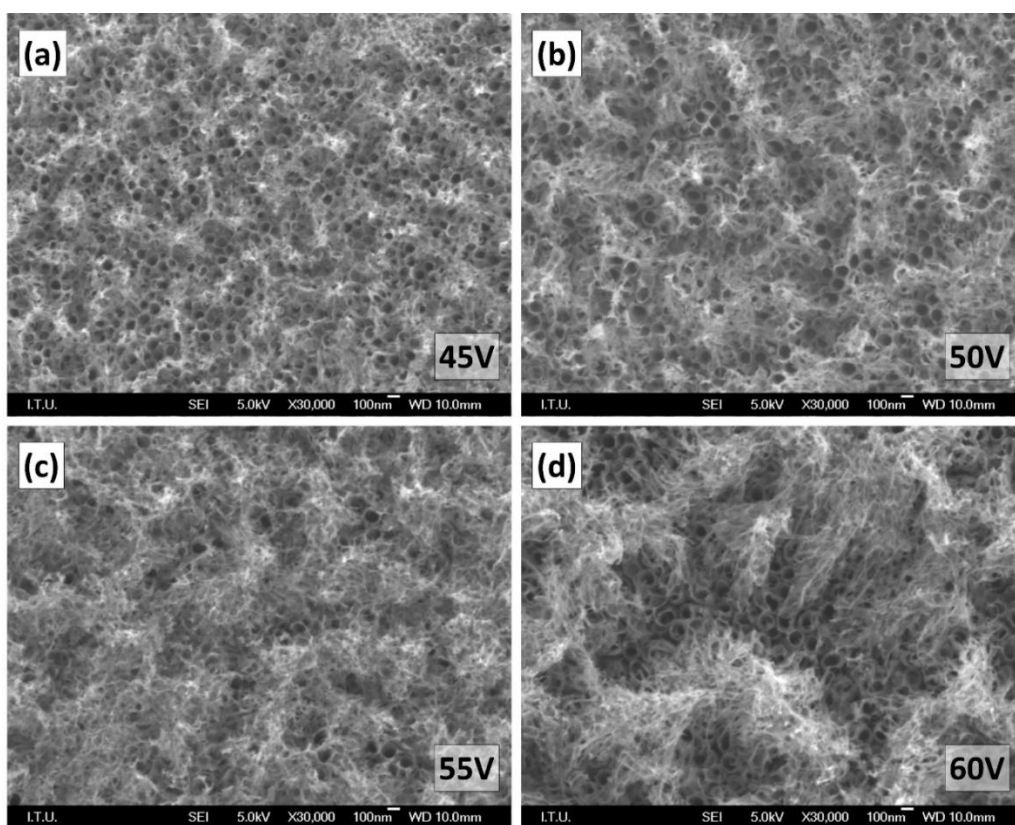


Figure 4.34 : FESEM images (at 30.000x magnification) showing the morphology of the samples anodized by applying different potentials at 30 °C for 20 min under 750 rpm stirring: (a) 45 V, (b) 50 V, (c) 55 V, (d) 60 V.

We knew that we could obtain an open-top nanotubular structure by anodizing at 50 V and 30 °C for 20 m under 750 rpm stirring from the previous experiments, and the same result was obtained in this set of experiments. The residues on the surface were previously evaluated to be the barrier oxide residues, but in this study, it was understood that the structure is an early phase of nanograss formation that started to form as a result of the dissolution of the nanotube tops (Figure 4.34(b) and Figure 4.35(b)). The nanotube surface produced under 45 V was clean, and the residues on the surface were rare and smaller than the sample surface anodized at 50 V (Figure

4.34(a) and Figure 4.35(a)). This observation verifies that the residues on the structures originate from nanograss. If the residues originated from the barrier oxide layer, the sample anodized at 45 V should have had more surface residue than the 50 V anodized sample, which is not valid. On the other hand, in the anodization performed at 55 V potential, the nanograss layer on the surface became denser, and the bundles formed as a result of chemical dissolution became larger (Figure 4.34(c) and Figure 4.35(c)). Furthermore, in the anodization performed at 60 V potential, the nanograss layer became even denser, and the nanograss bundles became largest (Figure 4.34(d) and Figure 4.35(d)).

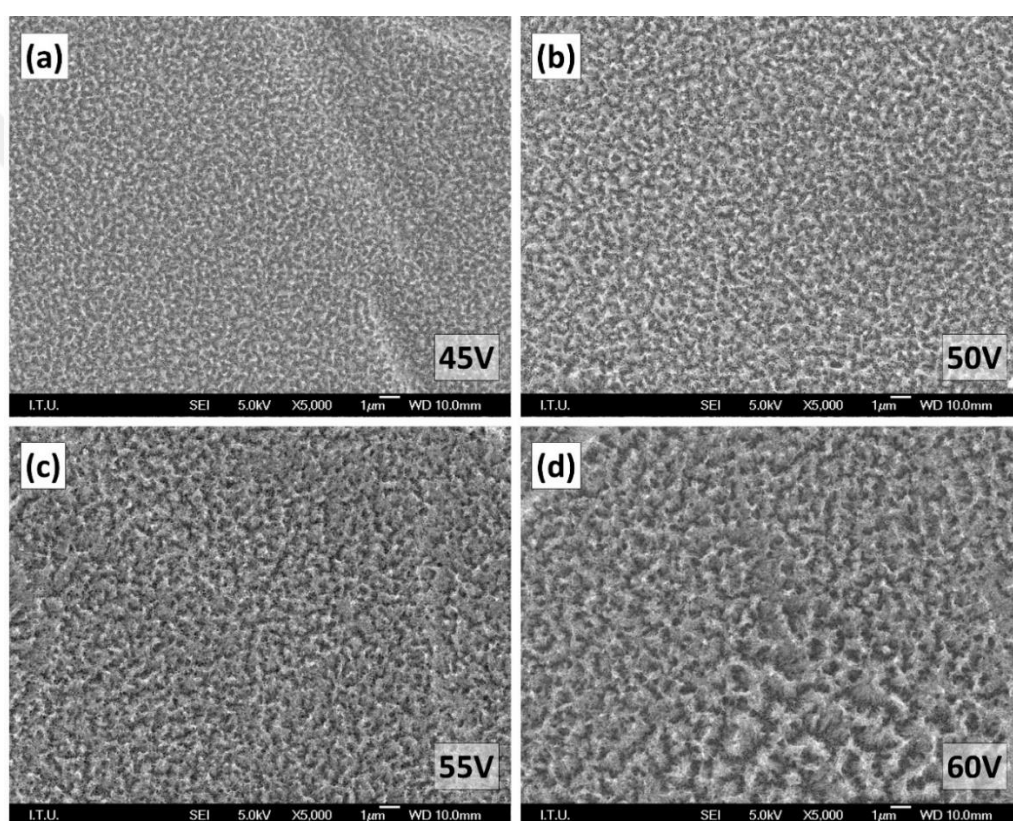


Figure 4.35 : FESEM images (at 5.000x magnification) showing the morphology of the samples anodized by applying different potentials at 30 °C for 20 min under 750 rpm stirring: (a) 45 V, (b) 50 V, (c) 55 V, (d) 60 V.

When the current density - time graph is examined, it is seen that the current density values (after the initial vertical descent) of the sample anodized at 60 V are almost twice that of the sample anodized at 45 V (Figure 4.33). Despite the current density (and thus the growth rate) almost doubling, the difference in morphology is not overly different, indicating that the anodization voltage affects the chemical dissolution process, but the effect is not very strong.

The anodization temperature is another critical parameter that strongly affects the process and significantly influences the current density and the chemical dissolution. The increase in the anodization temperature increases the mobility of the ionic species, causing the reactions to accelerate and the current density to increase. As it is well known, the increase in the current density causes the growth rate to increase. However, on the other hand, increasing the anodization temperature also negatively affects the growth process via increasing the chemical dissolution during anodization [37,75]. In order to observe the effect of temperature on the anodization current density and morphology, an experimental plan for examining the temperature range of 20 °C to 40 °C was prepared. As previously indicated under our reference parameters (50 V and 30 °C for 20 min under 750 rpm stirring), the barrier oxide film completely dissolves, leaving an open-top nanotube structure on the surface.

The current density values increase as the temperature increase as expected (Figure 4.36), and no inconsistency is observed on the current density - time plot.

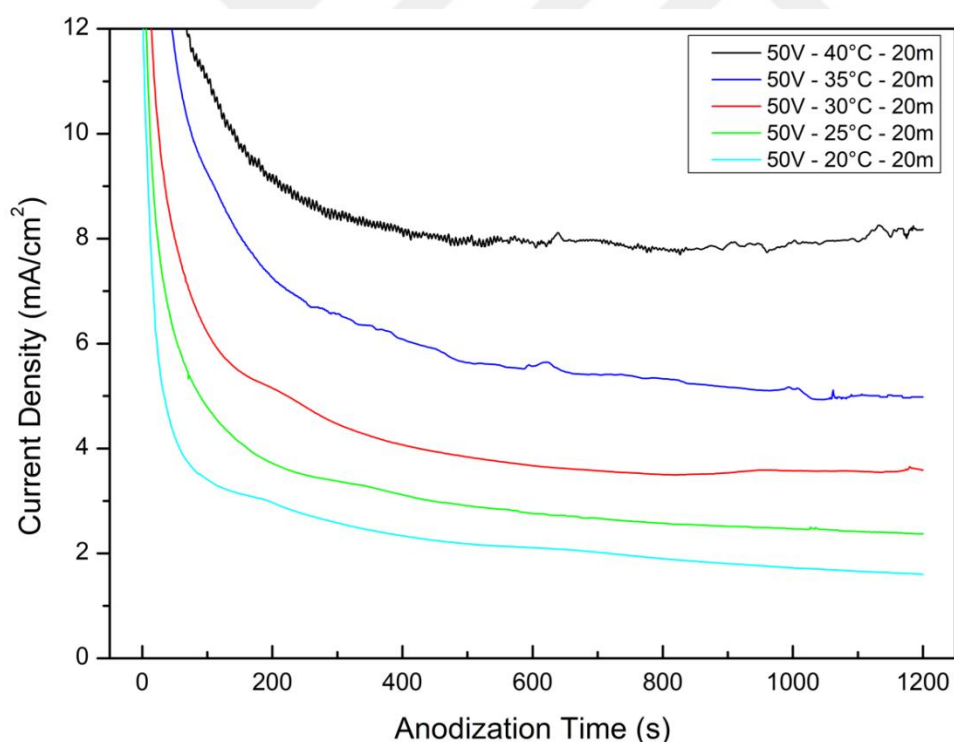


Figure 4.36 : Current density - time transient of samples anodized by applying 50 V at different temperatures (20 °C to 40 °C) for 20 min under 750 rpm stirring.

On the other hand, significant results were obtained when the surface morphologies of the anodized samples were examined. Surface FESEM images are presented at different magnifications (30.000x and 5.000x) in Figure 4.37 and Figure 4.38.

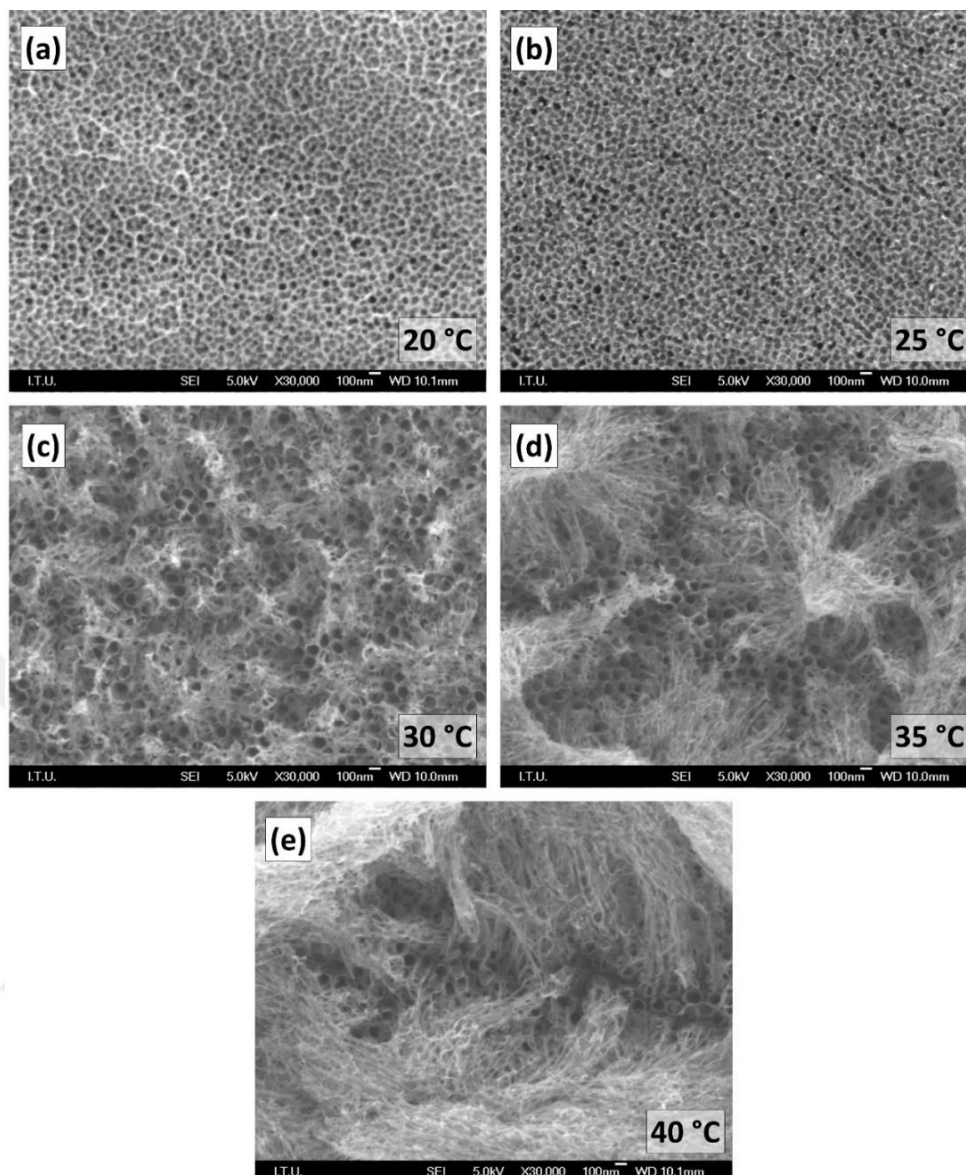


Figure 4.37 : FESEM images (at 30.000x magnification) showing morphology of the samples anodized by applying 50 V at different temperatures (20 °C to 40 °C) for 20 min under 750 rpm stirring: (a) 20 °C, (b) 25 °C, (c) 30 °C, (d) 35 °C, (e) 40 °C.

It was seen that the surface of the sample anodized at 20 °C was covered entirely with a compact barrier oxide layer (Figure 4.37(a) and Figure 4.38(a)). In the sample anodized at 25 °C, the surface was again completely covered with a barrier layer, but the structure of the layer was not as dense as the sample anodized at 20 °C (Figure 4.37(b) and Figure 4.38(b)).

In the sample anodized at 30 °C, nanograft formation was started, but the open-top nanotubes were still observed on the surface (Figure 4.37(c) and Figure 4.38(c)). On the surface of the sample anodized at 35 °C (Figure 4.37(d) and Figure 4.38(d)), the nanograft layer was denser, and the sizes of nanograft bundles were comparable

larger. On the sample surface anodized at 40 °C, the nanograss layer became highly dense and tangled due to excessive chemical dissolution. The uncontrolled growing layer completely covered the surface of the sample (Figure 4.37(e) and Figure 4.38(e)). In other words, it was observed that the morphology drastically varies depending on the anodization temperature.

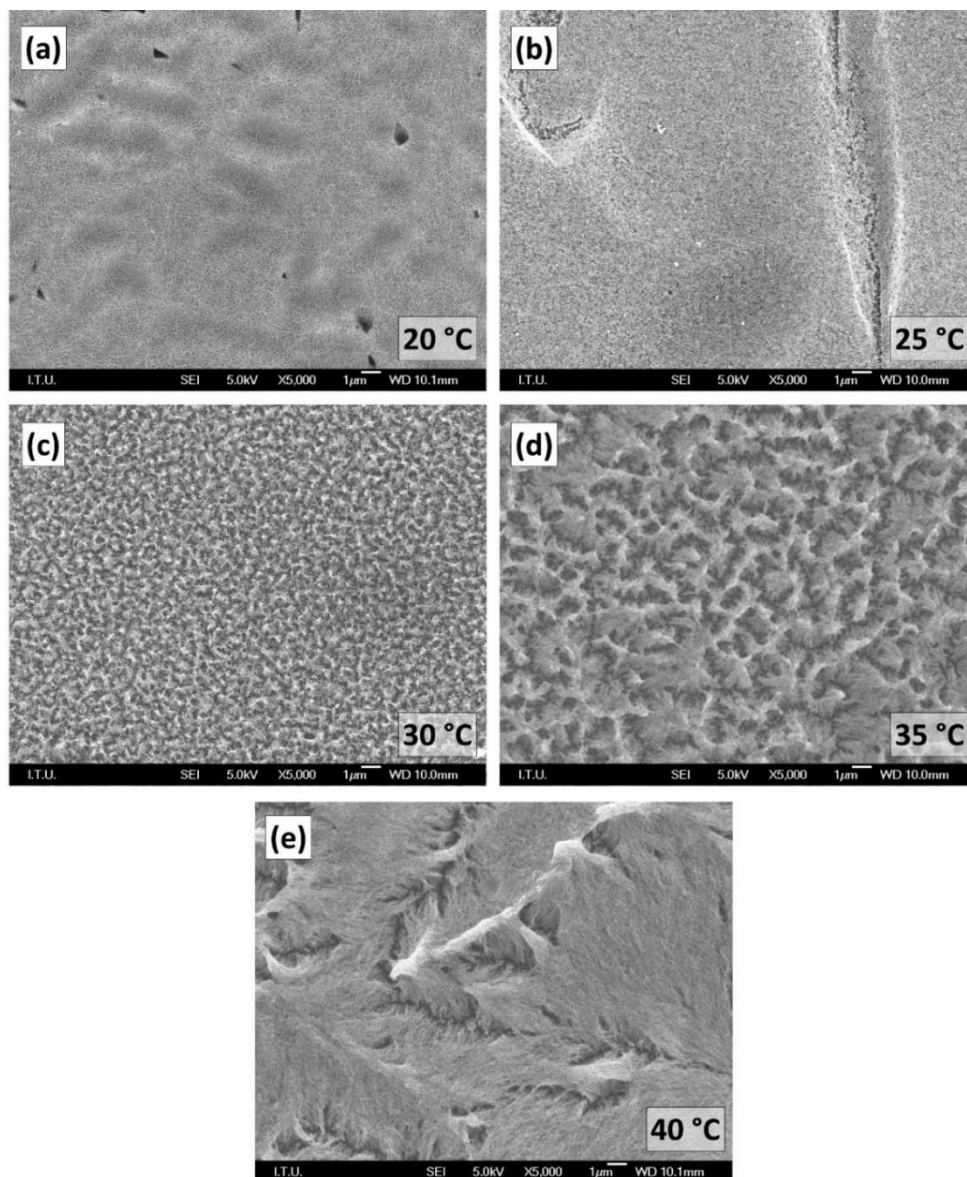


Figure 4.38 : FESEM images (at 5.000x magnification) showing morphology of the samples anodized by applying 50 V at different temperatures (20 °C to 40 °C) for 20 min under 750 rpm stirring: (a) 20 °C, (b) 25 °C, (c) 30 °C, (d) 35 °C, (e) 40 °C.

Another interesting result was revealed in the FESEM images taken from different sample parts, which were anodized at 50 V and 30 °C for 20 min under 750 rpm stirring. Electrolyte temperature was precisely controlled during anodization (± 0.1 °C). However, the atmospheric temperature of the glovebox where the anodization is

carried out was at the level of 22 °C. As seen in Figure 4.39, FESEM images taken from the middle and lower sections of the sample revealed identical morphologies, open-top nanotubes with some residue. However, when FESEM imaging was performed from the top region of the sample, which was very close to the electrolyte-atmosphere interface during anodization, it was seen that the surface is covered with a barrier layer, showing a different morphology (Figure 4.39(a) and (b)).

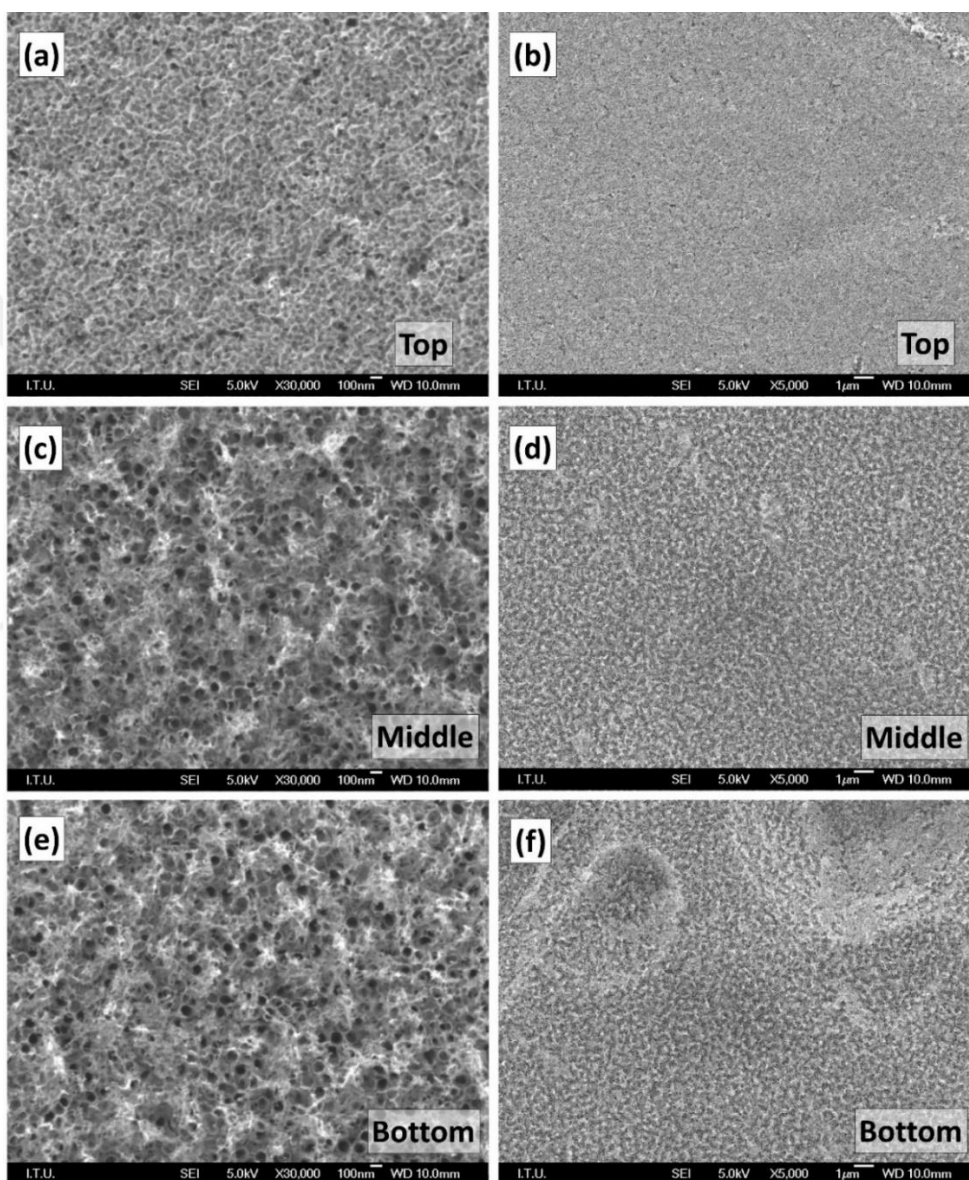


Figure 4.39 : FESEM images taken from different sections of the sample anodized at 50 V and 30 °C for 20 min under 750 rpm stirring: (a), (b) Top part; (c), (d) Middle part; (e), (f) Bottom part.

When the previous findings are evaluated, it can be said that the uppermost region of the sample behaved as if it had been anodized in a colder electrolyte. We think that a

slight temperature gradient occurred in the uppermost region of the electrolyte because the solution-atmosphere temperature difference is the cause of this observation.

In support of this finding, the results of anodization performed at 25 °C, the morphology of the uppermost section of the sample were negligibly different from other parts sample. Since the anodization and the ambient temperature were close to each other, the morphology difference remained at a negligible level. The effect that causes differentiation of morphology gets more vital as the difference between the anodization temperature and the atmospheric temperature increases. Considering this, in this study, where reproducibility is essential, all FESEM images were always performed from the middle region of the samples.

Similar to anodization potential, anodization temperature significantly affects the current density behavior (and growth rate). The current density level seen in anodization carried out at 40 °C was approximately three times the level of anodization carried out at 20 °C. The morphologies obtained in the anodization carried out at 20 °C and 40 °C under the same conditions were incomparably different. These results indicated the more prominent role of temperature on morphology.

A remarkable result appears when the effect of anodization temperature on current density and morphology is compared with voltage. The morphology difference between structures obtained by anodization at 30 °C and 35 °C resembles the morphology difference between structures obtained by anodization at 45 V and 60 V. It was revealed that anodization current density roughly doubled when the voltage was changed from 45 V to 60 V and increased roughly 1.5 times when the temperature was changed from 30 °C to 35 °C. To conclude, the temperature increase resulting in the same morphology change can only increase the current density by half of the voltage increase resulting in the same morphology change. The results of the experiments indicates that temperature is much more effective than the voltage on the chemical dissolution process and the morphology.

In the formation and growth kinetic studies, it was decided to use an often practiced value of 50 V anodization potential, as it was experimentally demonstrated that regular nanotube structures could be obtained using this parameter. On the other hand, anodization temperature was one of the main variables that strongly affected the chemical dissolution process during anodization.

4.1.5 Effects of anodization duration

It is well known that the main effect of the anodization duration is on the length of the nanotubes: As the anodization duration increases, the nanotube length increases [70]. However, as reported previously, nanotube growth is limited with the effect of chemical dissolution [25,48,57]. In addition, it has been reported in various studies that long anodization durations can cause nanograss formation on sample surfaces [29,32,93]. Although various studies show different surface morphologies are observed depending on the anodization duration, the duration-dependent surface morphologies have not been systematically investigated and clearly defined. An experimental plan was prepared to observe the effects of the anodization duration on the surface morphology.

The first set of experiments was conducted at 50 V and 30 °C for different durations from 5 min to 40 min under 750 rpm stirring. Since the behavior of anodization performed for 20 minutes using these parameters was known from previous experiments, it was used as a reference, and the morphologies formed as a result of anodization performed for shorter and longer durations were investigated. The surface morphologies formed after anodization experiments performed for different durations are presented in Figure 4.40 and Figure 4.41 at different magnifications

It was observed that the surface of the samples anodized for 5 min and 10 min was covered with a continuous barrier oxide layer. Although the morphologies of these layers were very similar, slight differences were observed in the structure of the films. It was seen that the pores on the barrier layer on the sample surface, which was anodized for 10 minutes, started to merge in comparison to the individual pores on the surface of the sample anodized for 5 minutes (Figure 4.40(a) and (b)). This difference supports that the barrier oxide layer was in the dissolution process, and the chemical dissolution progressed between 5 min to 10 min.

The 20 min anodized sample, which was used as the reference, had a clean surface with little nanograss structure on the nanotubes, as expected (Figure 4.40(c) and Figure 4.41(c)). However, on the surface of the sample, which was anodized for 40 minutes, a nanograss structure that had progressed to a certain level of dissolution was observed (Figure 4.40(c) and Figure 4.41(c)). In essence, it was deduced that the surface morphology during anodization progresses in the order of barrier layer, open

nanotubes, and nanoglass structure as the anodization duration increases, showing that these morphologies are successive processes.

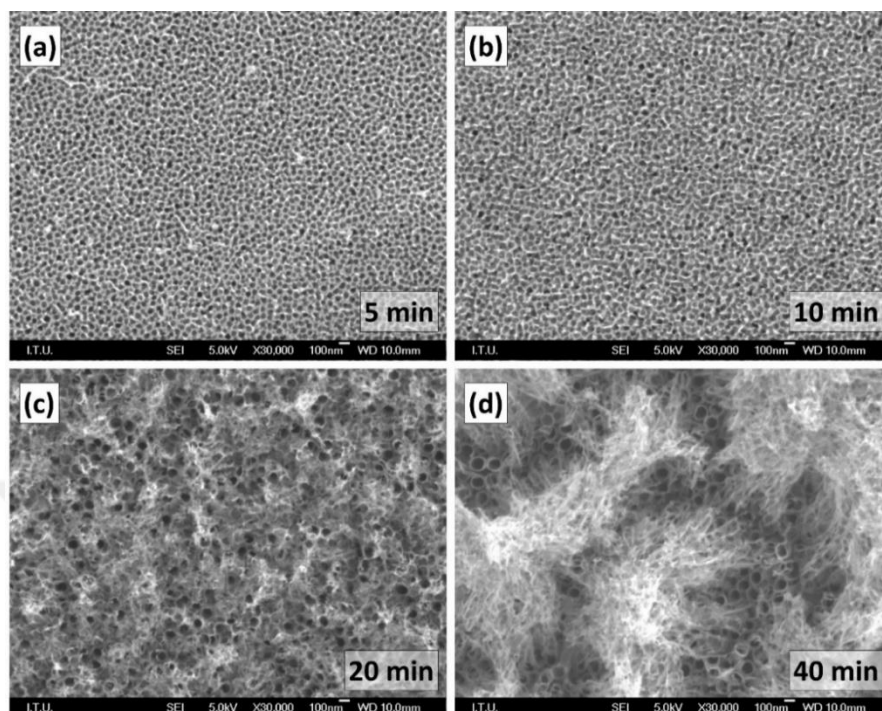


Figure 4.40 : FESEM images (at 30.000x magnification) showing the morphology of the samples anodized at 50 V and 30 °C for different durations under 750 rpm stirring: (a) 5 min, (b) 10 min, (c) 20 min, (d) 40 min.

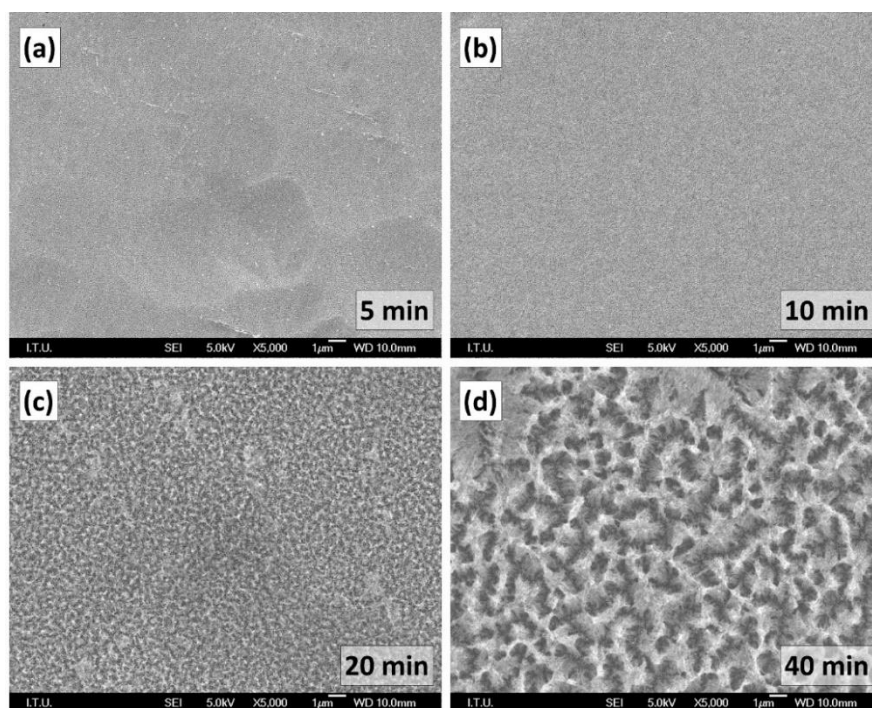


Figure 4.41 : FESEM images (at 5.000x magnification) showing the morphology of the samples anodized at 50 V and 30 °C for different durations under 750 rpm stirring: (a) 5 min, (b) 10 min, (c) 20 min, (d) 40 min.

In order to verify the successive morphological transformations, another time-dependent study was planned with employing 25 °C anodization temperature. Anodization experiments were conducted at 50 V and 25 °C for 20 min, 40 min, 60 min, and 120 min under 750 rpm stirring. In the sample anodized for 20 minutes, a barrier oxide layer whose structural integrity started to disrupt was observed on the surface (Figure 4.42(a) and Figure 4.43(a)). Nanograss formation had started, but open-top nanotubes were still visible on the surface of the sample anodized for 40 minutes (Figure 4.42(b) and Figure 4.43(b)).

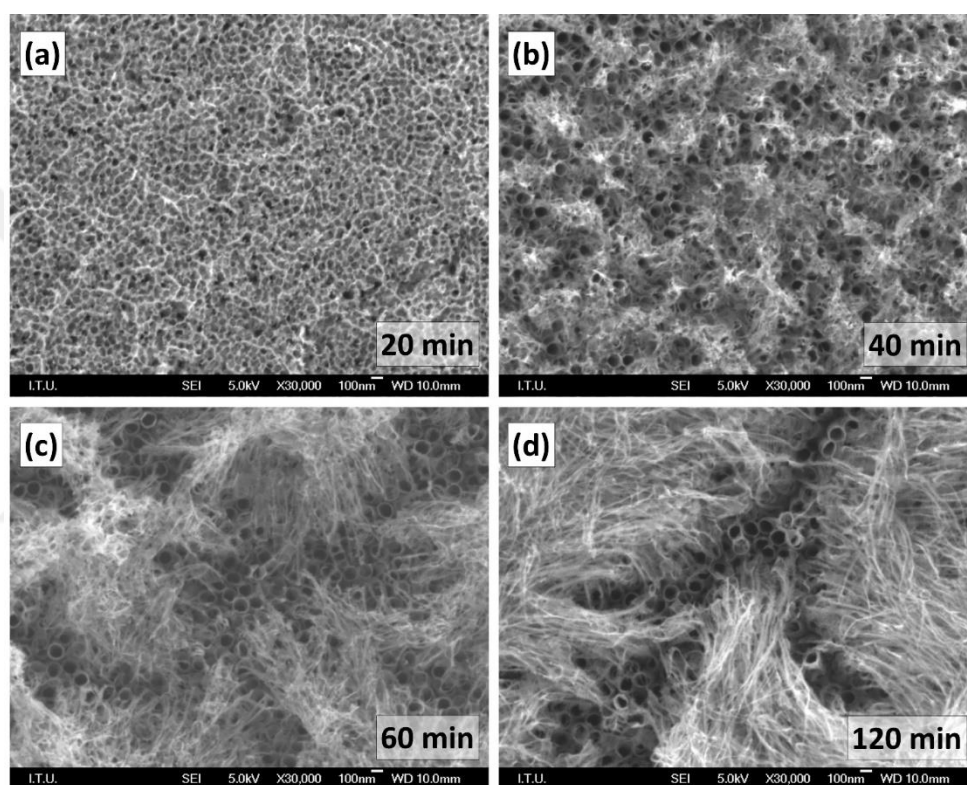


Figure 4.42 : FESEM images (at 30.000x magnification) showing the morphology of the samples anodized at 50 V and 25 °C for different durations under 750 rpm stirring: (a) 20 min, (b) 40 min, (c) 60 min, (d) 120 min.

In the case of 60 minutes anodization, the nanograss layer became denser, and bundles got larger (Figure 4.42(c) and Figure 4.43(c)). Moreover, in the sample anodized for 120 minutes, the nanograss layer became highly dense and wholly covered the nanotubes so that the nanotubes were not visible on the surface (Figure 4.42(d) and Figure 4.43(d)). Hence, in the anodization carried out at 25 °C, it was confirmed that the surface morphology changed from barrier oxide to open nanotubes and then to nanograss with increasing anodization duration.

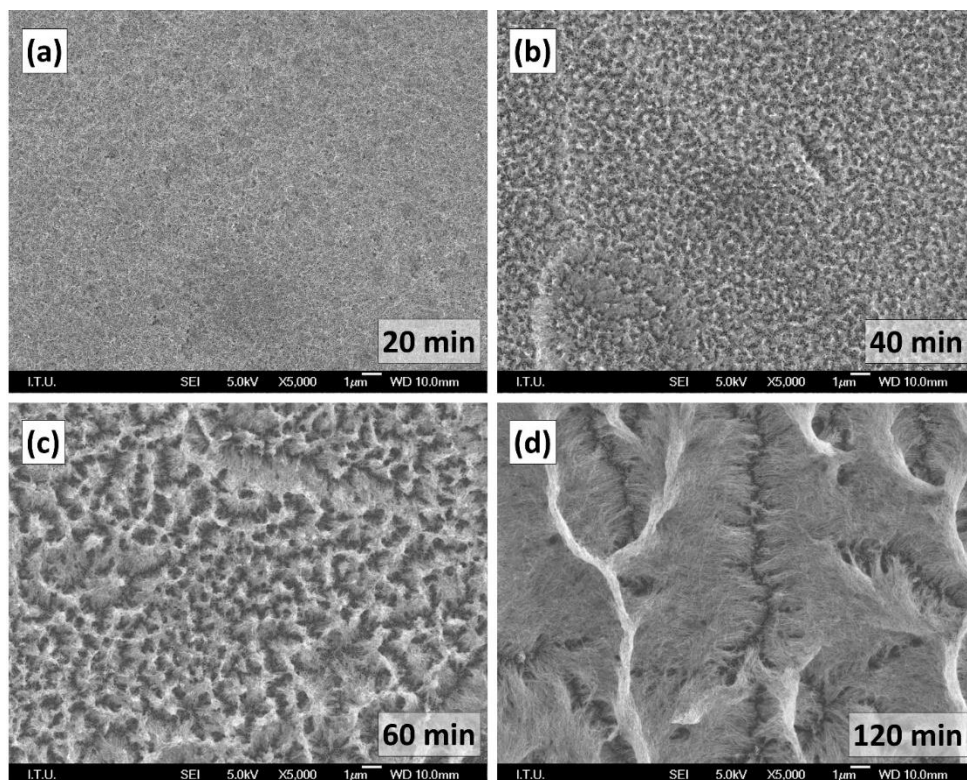


Figure 4.43 : FESEM images (at 5.000x magnification) showing the morphology of the samples anodized at 50 V and 25 °C for different durations under 750 rpm stirring: (a) 20 min, (b) 40 min, (c) 60 min, (d) 120 min.

In the experimental studies, it was seen that the nanotube surface morphology could be controlled by adjusting the anodization time and other parameters. Remarkably, similar surface morphologies were observed in 20 minutes anodization at 30 °C and 40 minutes anodization at 25 °C. A comprehensive study was planned considering that the anodization durations corresponding to morphological transformations may change systematically depending on the temperature. In the second part of the experimental studies of this thesis, which investigates the formation and growth kinetics of the nanotubes, morphological transformations depending on the anodization temperature and duration were studied in detail and presented in the relevant section.

4.1.6 Attempts to remove surface residues

In the studies investigating and optimizing the anodization parameters, many experiments were conducted using different parameters, and different surface morphologies were obtained. One of these surface morphologies is open-top nanotube structures without surface residue, the desired structure in most studies. Other obtained surface morphologies are barrier oxide layer or nanograss layer that entirely or

partially covers the surface, which is unwanted in most applications. Generally, long nanotubes are desired in most studies, and therefore, anodization durations are extended. For this reason, nanograss layers have been frequently encountered as irregular surface morphology and seen as a problem rather than a barrier oxide layer. In order to delay the formation of nanograss, several surface treatments and different modifications in the electrolyte composition have been tried and reported [29–34]. On the other hand, several studies have been carried out to remove the nanograss layer already formed on the surface [35,36]. In the experimental studies of this section, ultrasonication and stripping with scotch tape methods were tried for clearing the sample surface from barrier layer residues and so-formed nanograss.

Ultrasonication was applied in alcohol for 5 minutes to the samples whose surface was covered with different barrier layers (compact and loose) and nanograss. While there was no change in the morphology after ultrasonication in the sample with a compact surface barrier layer, the morphology of the sample with a loose surface barrier oxide layer was changed entirely after ultrasonication.

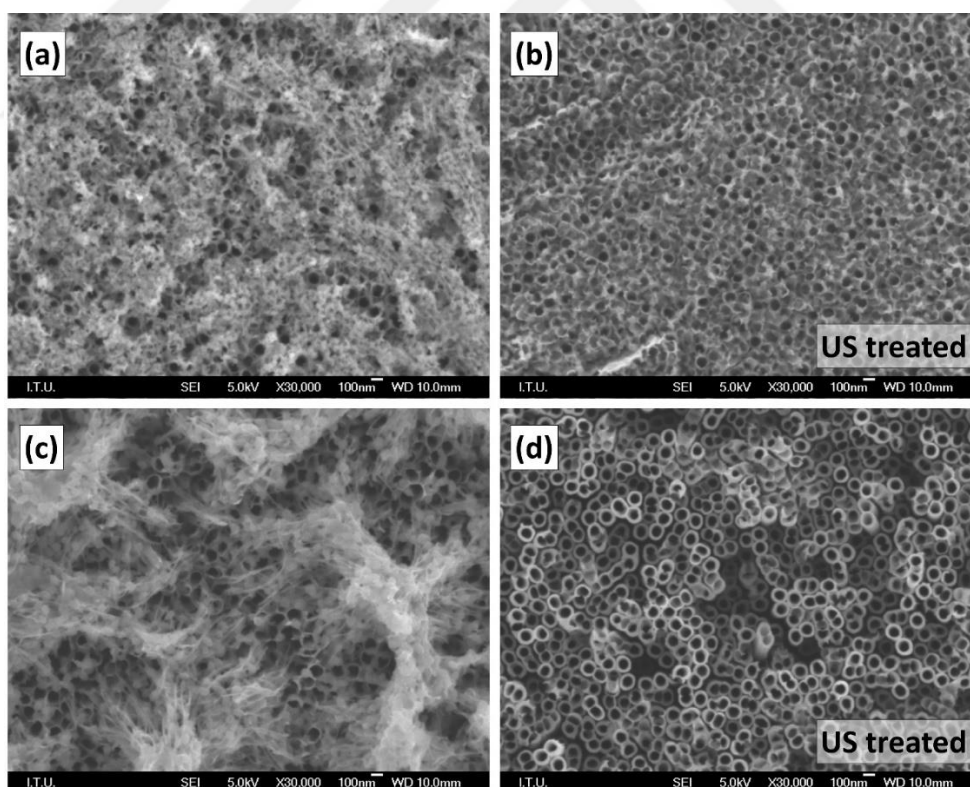


Figure 4.44 : FESEM images showing the effect of 5 minutes of ultrasonication on the morphology of the samples: (a) Barrier oxide morphology before US, (b) Barrier oxide morphology after US, (c) Nanograss morphology before US, (d) Nanograss morphology after US.

As the loose barrier layer was removed, open-top nanotubes became visible on the surface (Figure 4.44(a) and (b)). A similar result was obtained in the nanograss-coated sample, where the layer on the surface was completely removed after 5 minutes of ultrasonication (Figure 4.44(c) and (d)).

Although it was possible to remove the surface residues such as barrier layer or nanograss structure by ultrasonic treatment for 5 minutes, ultrasonication had several adverse effects. Breaking of the nanotubes, especially at the upper parts, was observed from the tilted FESEM image ((Figure 4.45(a)). The breakage of the nanotubes can also be understood from morphological examinations. As explained in the previous sections, the lower regions of the nanotubes have a thicker wall thickness, while the near-surface parts are thinner (V-shaped) [73]. With the breakage of the nanotubes' upperparts, thicker wall sections became apparent (Figure 4.44(d)). Another problem encountered during ultrasonication is separating the nanotube film from the surface and even inversion of the separated film (Figure 4.45(b)).

Ultrasonication removes the surface residues of the sample but causes severe damage to the nanotube structure. In this study, ultrasonication for shorter durations was also performed. Although the amount of damage on the nanotube film was reduced in shorter ultrasonication operations, similar problems continued to be encountered.

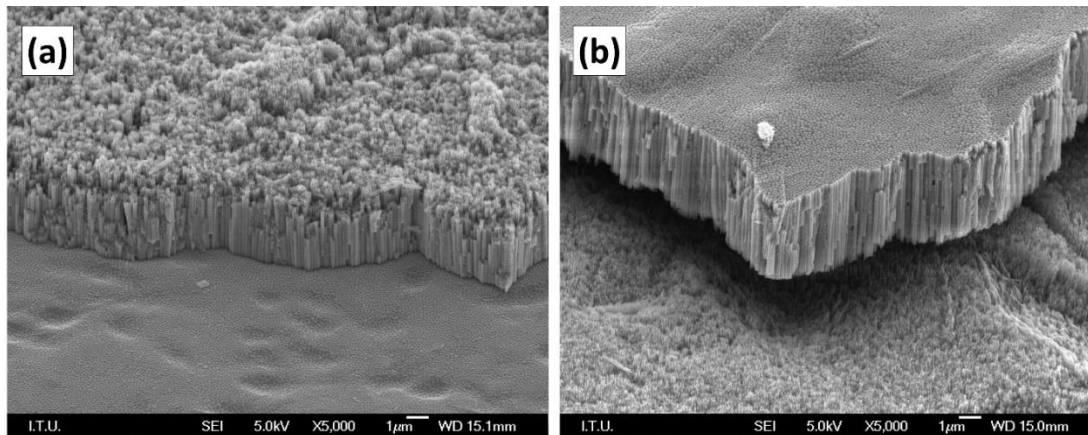


Figure 4.45 : FESEM images showing the adverse effects of ultrasonication on the sample surface: (a) Example of damaged nanotube film due to US treatment, (b) Example of an inverted nanotube film due to US treatment.

As another experimental study, the surfaces of the samples, which were covered with a loose barrier layer, the early phase of nanograss, and dense nanograss, were tried to be cleaned using scotch tape. It was possible to clean the surface residues with tape in all three samples (Figure 4.46). However, this cleaning only took place partially on the

sample surface. The residues in some parts of the sample remained on the tape, while the residues in other parts remained still on the sample surface.

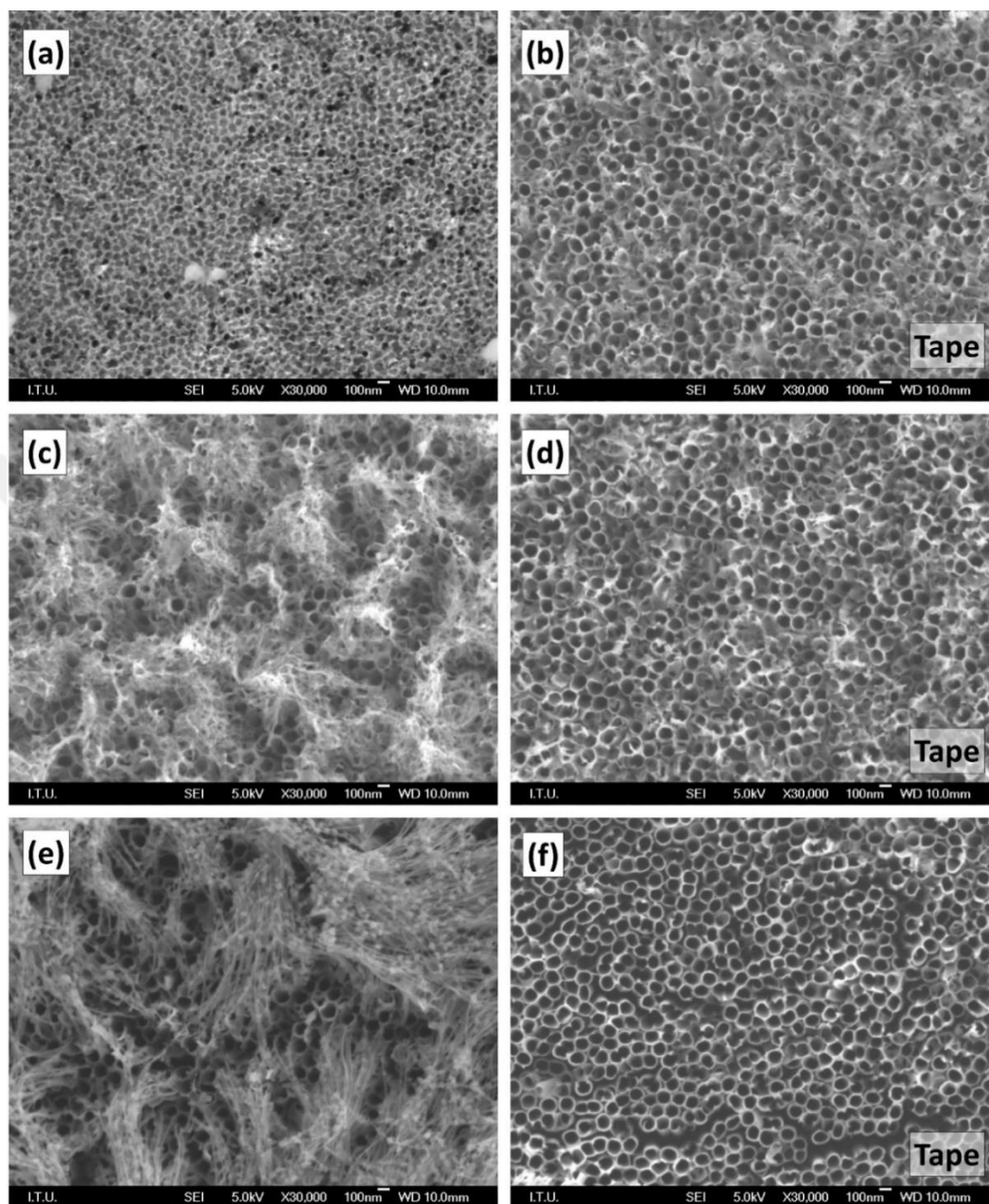


Figure 4.46 : FESEM images showing the effect of stripping with a scotch tape on the morphology of the samples: (a) Barrier oxide morphology before tape, (b) Barrier oxide morphology after tape, (c) Nanograss morphology before tape, (d) Nanograss morphology after tape, (e) Dense nanograss morphology before tape, (f) Dense nanograss morphology after tape.

Tape tests were performed on the marked areas on the samples to observe the tests' effectiveness. In many samples, only partially cleaning of the surface could be achieved in scotch tape treatments. The FESEM image of a marked region on a sample having a dense nanograss layer (Figure 4.47(a)) and the FESEM image of the same

region after scotch tape treatment (Figure 4.47(b)) are presented in Figure 4.47, as an example of partial surface cleaning. In addition, in some cases, the nanotube film was also removed from the sample surface.

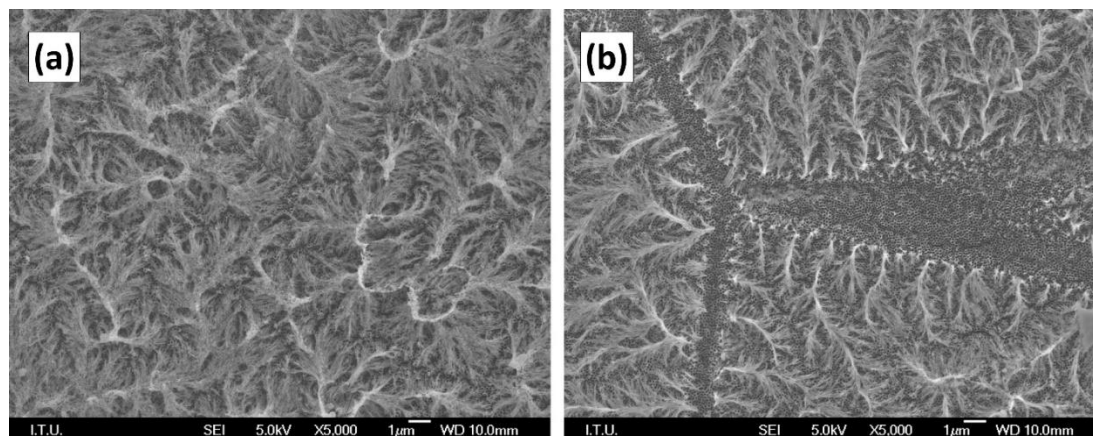


Figure 4.47 : FESEM images showing the negative effect of stripping with a scotch tape on the sample surface: (a) A dense nanograss morphology before stripping with scotch tape, (b) Example of a failure on the dense nanograss layer due to uneven adhesion of the tape.

Both ultrasonication and stripping with tape methods are not versatile due to their impracticality, difficulty in control, poor reproducibility, and most importantly, the severe damage they leave on the sample. For this reason, it has only been tried in some experimental studies and has not been applied again. On the other hand, it was a beneficial study providing information about the nanotube formation and growth behaviors under the surface layers, which will be detailed in the next section.

In addition, while the studies on removing the so-formed surface residues are presented in this section, prevention of surface residues by controlling the anodization process will be discussed in the following section, where formation and growth kinetics studies are investigated.

4.2 Investigation of Formation and Growth Kinetics of the TiO₂ Nanotubes

In the second part of experimental studies, the formation and growth processes of TiO₂ nanotubes were investigated, and a kinetic model that examines the growth process under different stages was produced.

In this part, where reproducibility was critical and could be significantly affected by small changes in the parameters, all solution preparation and anodization processes were carried out inside a glovebox. The anodization parameters optimized in the first

part of the experimental study were utilized. In order for the reactions and morphological transformations to occur at a slower pace and to be monitored fluently, the fluoride concentration in the electrolyte was reduced by half compared to the first part. The anodization electrolyte containing 0.3 wt % NH_4F and 1 vol % H_2O in ethylene glycol was freshly prepared before each experiment and used only once to eliminate the aging of the electrolyte. A two-step anodization procedure that optimized in the first part was used in the experiments. Anodization experiments in the formation and growth kinetics studies were performed at 50 V and under 750 rpm stirring, which was optimized and practiced in the previous part.

We determined that the nanotube films obtained during experimental studies are formed in 3 primary morphologies, and these morphologies follow each other sequentially: initial barrier oxide layer, open surface nanotubes, and nanograss layer. The different structures of the initial barrier layer and the different conditions of the nanograss layer encountered during experiments allowed us to understand that chemical dissolution processes systematically affect the morphology during anodization.

In this section, a kinetic model is proposed to explain the growth of nanotubes and morphological transitions based on electrochemical growth and chemical dissolution. In the suggested model, the kinetics of titania nanotube growth in ethylene glycol-based electrolytes was investigated using three successive stages for the growth process. Morphological transitions and growth kinetics during anodization were investigated individually for all stages. In Stage 1, the growth of nanotubes under a gradually dissolving initial barrier oxide layer was investigated. Stage 2 is defined as the short period where nanopore/nanotube transition occurs after the complete dissolution of the initial barrier oxide. In Stage 3, nanotube growth kinetics was examined during nanograss formation and progression. The kinetic model was extrapolated for application at different temperatures, and the compatibility of theoretical and experimental values was verified by anodization.

4.2.1 Stage 1

In this study, Stage 1 have been defined as the period which includes initial barrier oxide formation, pore initiation, and nanotube growth under gradually dissolving initial barrier oxide.

4.2.1.1 Morphology and growth mode in Stage 1

Titanium foils were anodized for 5, 15, and 30 sec at 25 °C (under the anodization conditions stated in the experimental section) to investigate the initial barrier oxide formation, pore initiation, and early growth phase of nanotubes. In Figure 4.48, the early period of surface morphologies and time-dependent current variations are presented.

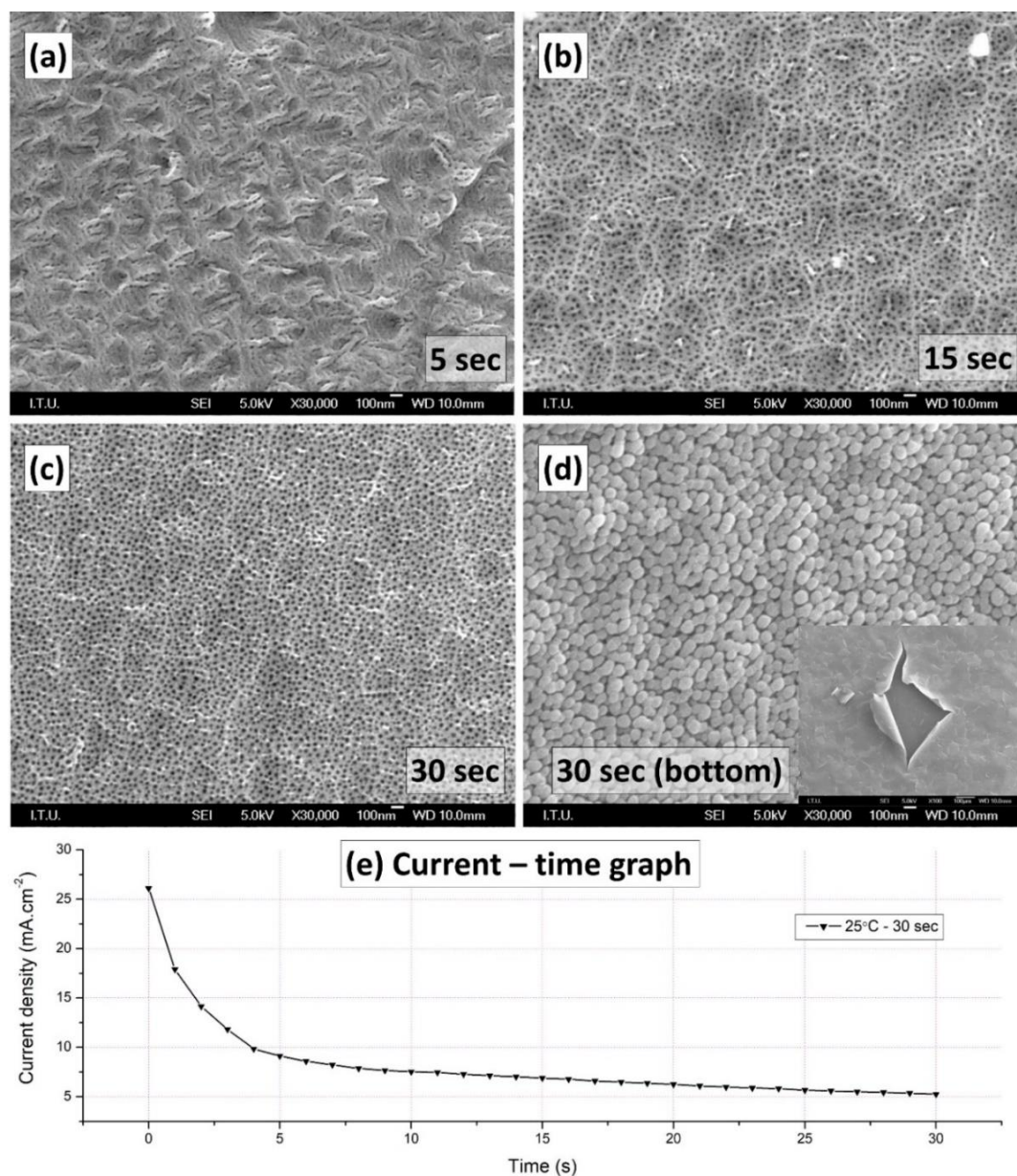


Figure 4.48 : FESEM images showing the early period of surface morphology of samples anodized at 25 °C for (a) 5 sec, (b) 15 sec, (c) 30 sec, (d) Bottom view of 30 sec anodized nanotube film, (e) Time-dependent current density transient for 30 sec anodization.

As can be followed from the current-time graph (Figure 4.48(e)), the sharp decay in the first few seconds indicates the anodic barrier oxide formation. In fluoride-free electrolytes, the anodic barrier oxide film formed on titanium has a particular thickness, which is linearly dependent on the applied potential, and it is usually in a range of 1-3 nm.V⁻¹ depending on other anodization parameters [16]. In the case of anodization performed in fluoride-containing electrolytes, barrier oxide formation kinetics are similar to fluoride-free electrolytes; however, this time, pit formation on the oxide also starts almost simultaneously with a momentary delay. Pit formation disrupts the passive oxide film and causes a leveling of current within a few seconds (Figure 4.48(e)). Since the pore initiation process interferes with the initial barrier oxide formation mechanism and affects current transient, it is difficult to estimate the exact thickness of the initial barrier oxide layer theoretically.

Pit formation (pore initiation points) on the initial barrier oxide was observed on the sample anodized for 5 sec (Figure 4.48(a)). The density of pore initiation pits on the initial barrier oxide increased considerably up to 30 sec of anodization time (Figure 4.48(a), (b), and (c)). Besides, a clear tubular bottom structure (sized approximately 100 nm in diameter) was observed at the backside of lifted oxide film on the sample anodized for 30 sec (Figure 4.48(d)), demonstrating that ordered nanotubular formation under initial barrier oxide occurs in the early periods of the anodization. Additionally, the sharp change in the slope of the current-time graph at close to 5 sec may indicate the initiation of nanotubes below the barrier layer (Figure 4.48(e)).

At Stage 1, the extension of anodization duration resulted in an increase in nanotube film thickness along with a distinct change in the morphology of the top barrier layer (Figure 4.49). In the sample anodized for 80 min (at 25 °C), the disintegration of the initial barrier oxide was evident when compared to the sample anodized for 20 min (at 25 °C) (Figure 4.49(a) and (b)). For the sample anodized for 80 min, regular nanotubes were slightly visible in the regions where the initial barrier oxide is partially dissolved (Figure 4.49(b)). When the anodization duration was further increased, and initial barrier oxide was dissolved entirely, an open-top ordered structure was observed on the sample (Figure 4.50(a) and (b)), which is considered as the end of Stage 1 in this model.

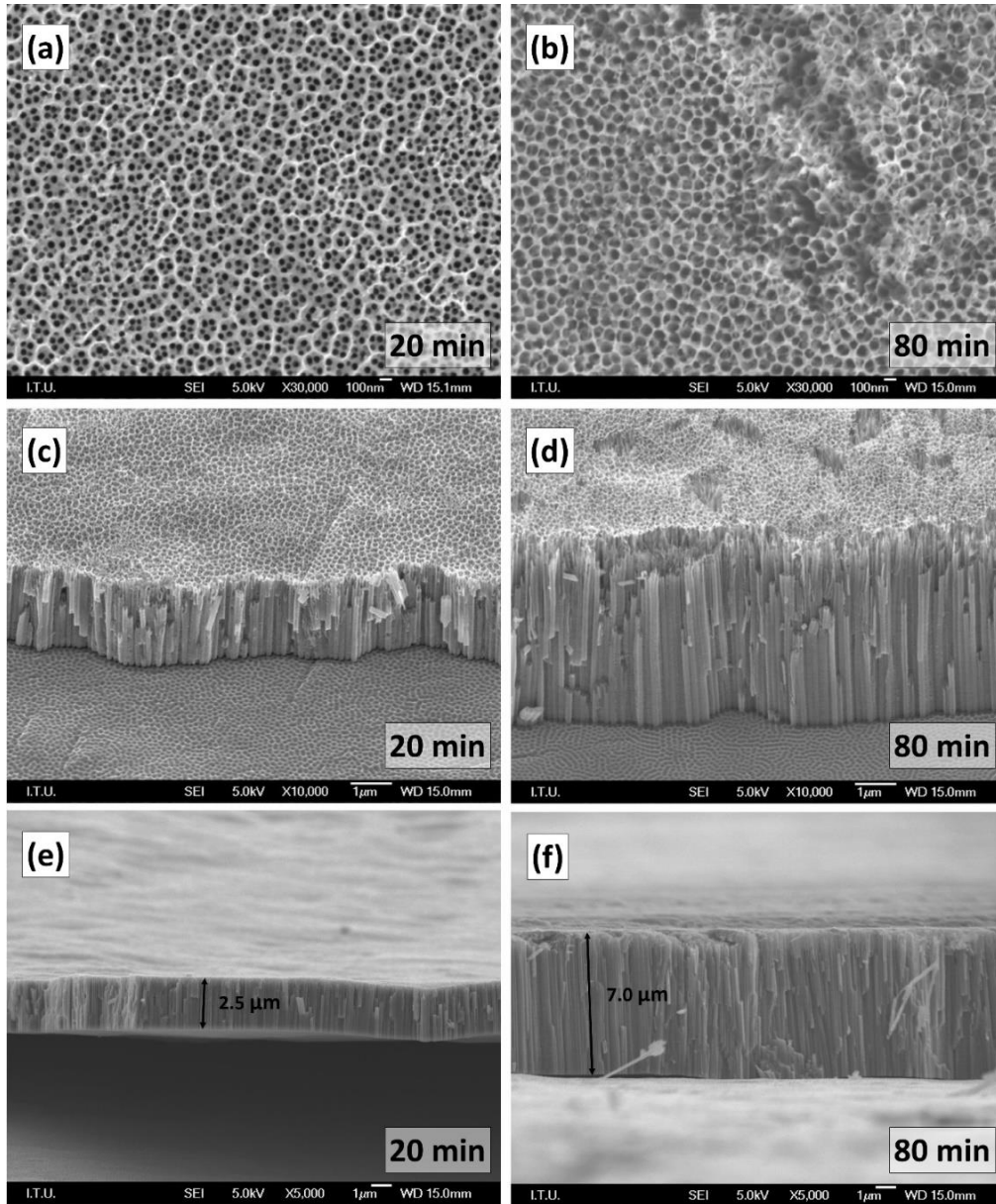


Figure 4.49 : FESEM images top view of (a) 20 min, (b) 80 min; tilted view of (c) 20 min, (d) 80 min; cross-sectional view of (e) 20 min, (f) 80 min anodized samples at 25 °C.

The chemical dissolution process in titanium anodization has a crucial effect on nanotube growth and morphology. On the one hand, field-assisted chemical dissolution at the tube base is the critical factor for nanotubular growth; but on the other hand, the chemical dissolution process on the top of the nanotubes is the limiting factor for nanotube growth. Initial barrier oxide has a protective feature during nanotube growth, and the complete dissolution of the layer leaves the tube tops unprotected against chemical attack. The chemical dissolution rate of initial barrier oxide varies depending on the anodization conditions and electrolyte properties; especially, viscosity and pH of the electrolyte significantly affect the chemical

dissolution rate. High pH and viscosity; reduce the chemical dissolving power of the electrolyte, decrease the chemical dissolution rate of initial barrier oxide, and promotes longer nanotubes [22,25].

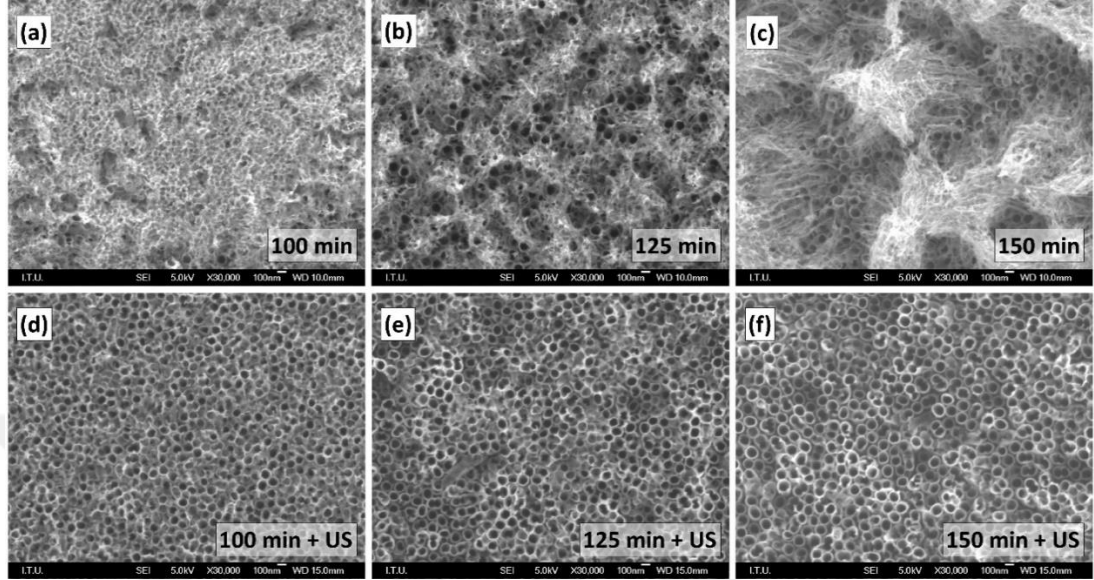


Figure 4.50 : FESEM images showing the morphology of the samples anodized at 25 °C for (a) 100 min (last period of barrier oxide dissolution), (b) 125 min (nanopores with minimal barrier oxide residue), (c) 150 min (early period of nanoglass formation). FESEM images of the same samples ultrasonically cleaned for 2 min to remove top residues (d) 100 min + US (nanopores), (e) 125 min + US (nanopore-nanotube transition), (f) 150 min + US (nanotubes).

Initial barrier oxide formed at a particular thickness according to the anodizing condition was expected to dissolve entirely in a specific time, depending on the chemical dissolving power of the electrolyte. It was experimentally observed that the total dissolution time of the initial barrier oxide layer during anodization performed at 25 °C was within the range of 100-150 min (Figure 4.50(a), (b), and (c)). The initial barrier oxide dissolution process starts at the beginning of the anodization and continues until the barrier layer is completely dissolved. The dissolution process is accompanied by field-assisted oxide growth (nanotube growth), which occurs at the bottom, underneath the initial barrier oxide layer throughout the dissolution.

4.2.1.2 Kinetics of growth in Stage 1

The field-assisted growth rate of nanotubes below the top barrier can be calculated with the following procedure. The thickness of homogeneous anodic oxide films can be calculated using the total charge passed during the anodization [26]. The theoretical thickness of the homogenous amorphous oxide film (L) grown on titanium during

anodization under 100% current efficiency (considering 4 electron reactions) can be obtained with the equation [94]:

$$L = \frac{QM_{(TiO_2)}}{\rho_{(TiO_2)}4F} \quad (4.1)$$

In this equation, Q is the total charge consumed per unit area during oxidation ($C\ cm^{-2}$), $M_{(TiO_2)}$ is the molar mass of TiO_2 ($79.88\ g\ mol^{-1}$), $\rho_{(TiO_2)}$ is the density of amorphous TiO_2 ($3.1\ g\ cm^{-3}$), and F is the Faraday constant ($96485\ C\ mol^{-1}$). The homogenous anodic oxide film growth rate (μm per coulomb) calculated using the above parameters is $0.667\ \mu m\ C^{-1}\ cm^2$.

Volume expansion during anodic oxidation is linked to the Pilling-Bedworth ratio (PBR) [94]. In equation 4.1, PBR is included in $\rho_{(TiO_2)}$ as the density of the oxide is related to volume expansion during anodization. For a homogeneous, defect-free titanium oxide with a density of $3.1\ g\ cm^{-3}$, the PBR value is determined as 2.43 [94]. However, different PBR values for nanotubular titania have been reported in the literature. There are findings in the literature that demonstrate PBR value may change depending on the anodization conditions, and thus, experimental determination of growth rate and PBR is recommended for accurate analysis at the working conditions [95]. Equation 4.1 shows that oxide thickness is directly proportional to total charge, but as the volume expansion during anodization may change depending on the conditions, it is not practical to use this equation to obtain the growth rate and thickness of the nanotubular oxide film. Field-assisted oxide growth rate (μm per coulomb) should be determined experimentally for the specific anodization condition, and then $\rho_{(TiO_2)}$ and PBR of the formed oxide can be calculated using equation 4.1.

Titanium samples were anodized at $25\ ^\circ C$ for different durations (20 min and 80 min) remaining in Stage 1 to determine field-assisted growth rate ($\mu m\ C^{-1}\ cm^2$). Titania nanotube thicknesses were observed by FESEM investigations (Figure 4.49(e) and (f)), and field-assisted growth rate ($\mu m\ C^{-1}\ cm^2$) was determined using charge density data ($C\ cm^{-2}$) recorded during anodization (Table 4.2). In both anodized samples (20 min and 80 min) average growth rate of $\sim 0.7\ \mu m\ C^{-1}\ cm^2$ was obtained from experimental data. The field-assisted growth rate of the oxide (per coulomb) and, thus, the volume expansion (PBR) of the oxide showed no change during the anodization under the same conditions (Table 4.2). When nanotube film thicknesses were compared with the calculated theoretical thickness for homogenous amorphous anodic

titania using equation 4.1; the field-assisted growth rate was 5% more than the theoretical growth rate of the homogenous amorphous titania, which is compatible with the flow model growth.

Table 4.2 : Experimental data of the samples anodized at 25 °C and 5 °C: anodization duration, total charge density during anodization, and final nanotube length. The growth rate of the tubes is obtained by dividing the final nanotube length (L) by total charge density (Q). According to the suggested model, growth mode indicates the corresponding growth stage (Stage 1: barrier oxide top layer, Stage 3: nanograss top layer). The aspect ratio of the nanotubes is calculated using an average pore size of 100 nm.

Anodization Temperature (°C)	Anodization Duration (t) (min)	Total Charge Density (Q) (C cm ⁻²)	Final Nanotube Length (L) (μm)	Growth Rate of Tubes (GR) (μm C ⁻¹ cm ²)	Aspect Ratio	Growth Mode
25	20	3.58	2.5 (±0.1)	0.698 (±0.028)	25 (±1)	Stage 1
	80	9.93	7.0 (±0.2)	0.705 (±0.020)	70 (±2)	
	240	22.78	13.8 (±0.4)	0.606 (±0.017)	138 (±4)	Stage 3
	390	33.19	18.2 (±0.4)	0.548 (±0.012)	182 (±4)	
	540	42.95	22.1 (±0.5)	0.515 (±0.012)	221 (±5)	
5	90	3.71	2.6 (±0.1)	0.701 (±0.027)	26 (±1)	Stage 1
	240	7.76	5.4 (±0.2)	0.696 (±0.026)	54 (±1)	
	660	15.87	9.6 (±0.3)	0.605 (±0.019)	97 (±3)	Stage 3
	1020	22.10	11.7 (±0.3)	0.529 (±0.013)	117 (±3)	
	1440	28.64	13.7 (±0.4)	0.478 (±0.014)	137 (±4)	

In brief, during Stage 1, we determined that the field-assisted oxide growth of the nanotubes occurs at a constant rate (μm C⁻¹ cm²) at the bottom, under the gradually dissolving and still protective initial barrier oxide layer.

4.2.2 Stage 2

As previously stated, we have defined this stage as the short period after the initial barrier oxide layer is entirely dissolved in which open tube top ordered nanotubes are seen, and nanopore/nanotube transition occurs.

In the literature, nanopore to nanotube transition is attributed to the high dissolution tendency of fluoride-rich layer (FRL) accumulated at the outer parts of the tube walls

and triple junction points between the pores [90]. The nanopore to nanotube transition sequence is presented by using samples anodized for 100, 125, and 150 min (at 25 °C) with and without ultrasonication in ethanol (Figure 4.50). As can be observed in Figure 4.50(a) and Figure 4.50(d), an ordered nanoporous structure was present under thin residue of the barrier oxide layer, which was revealed clearly in the ultrasonicated sample surface. Limited contact with the electrolyte protects the tube tops and FRL layer from chemical attack. After the complete dissolution of the protective layer, the sensitive FRL layer (at pore junctions and outer parts of tube walls) starts to dissolve primarily since the inner part of the tube walls and tube tops are more resistant to chemical dissolution with their lower fluoride content [90]. After FRL dissolution, ordered nanotubes were seen on the surface (Figure 4.50(b) and (e)). In prolonged durations, tube tops also started to weaken because of the chemical dissolution and nanograss formation that occurred on the film (Figure 4.50(c) and (f)).

As Stage 2 is the sudden transition phase between Stage 1 and Stage 3, it was ignored in the kinetic calculations.

4.2.3 Stage 3

We have defined Stage 3 as the period for the chemical dissolution of the tube tops and the initiation and progress of nanograss formation. In this part, the growth of the nanotube film due to field-assisted formation and shortening of the film because of the chemical dissolution were examined together.

4.2.3.1 Morphology and growth mode in Stage 3

It is known that titania nanotubes are vulnerable to chemical dissolution and tube tops have to be protected to obtain longer nanotubes [96]. Initial barrier oxide acts as a protective film on the nanotubes and enables efficient growth during Stage 1. In extended anodization duration, after the protective top layer (initial barrier oxide) is completely dissolved, dissolution of the nanotubes starts, and a weaker zone rapidly occurs at the upper part of the nanotubes. As the chemical dissolution continues, weakened parts become unable to carry their weight and collapse onto each other leaving a disordered structure (nanograss) on the nanotube film [29]. The early period of the nanograss formation was seen in the sample anodized for 150 min at 25 °C (Figure 4.50(c)). Thinned and collapsed nanotube residues (upper parts) began to accumulate on the surface in bundles. Figure 4.51 shows the evolution of nanograss

structure on samples anodized for 4 h, 6.5 h, and 9 h (at 25 °C). Extending the anodization duration caused the chemically thinned zone (upper parts of the tubes) to shift down due to chemical dissolution; and the collapsing of the nanotubes continued cumulatively, forming a denser nanograss layer on the surface (Figure 4.51(a), (b) and (c)). Besides, as weakened parts collapsed and formed nanograss, nanotubes became shorter in length. Therefore, this process can also be defined as the shortening of the nanotubes because of chemical dissolution. Yasuda et al. showed that nanotube length during anodization is directly proportional to anodic charge up to a certain length that exhibits a decrease after reaching this specific length [97]. They attributed this observation to the chemical dissolution of the tubes but did not consider the hindering dissolution effect of the top barrier layer.

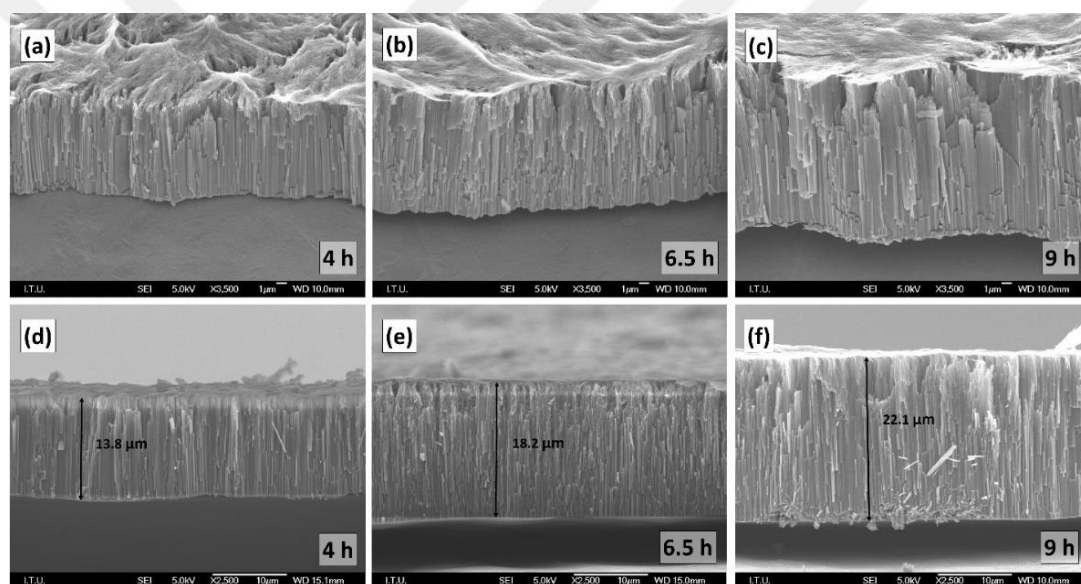


Figure 4.51 : FESEM images showing morphology and thickness of the samples anodized at 25 °C for (a), (d) 4h; (b), (e) 6.5h; (c), (f) 9h in Stage 3. The final thickness of the TiO₂ nanotube films is shown in the cross-sectional view.

Table 4.2 shows the experimental data of the samples anodized at 25 °C and 5 °C for different durations. When the growth rate of the nanotubes in Stage 3 was calculated using the same procedure as for Stage 1, a significant decrease in the growth efficiency was observed (Table 4.2). This result indicates the necessity of using different approaches for different stages of growth. Therefore, growth kinetics in Stage 3 should be investigated from a different perspective considering the shortening of the tubes because of the nanograss formation. In Stage 3, field-assisted growth continues at the bottom with the same efficiency and rate (per coulomb) ($\mu\text{m C}^{-1} \text{cm}^2$) as in Stage 1. However, the simultaneous shortening of the tubes because of the chemical dissolution

occurs at the top at a constant rate (per time) (nm min^{-1}), which varies depending on the anodization electrolyte properties and conditions.

4.2.3.2 Kinetics of growth in Stage 3

When the findings were compiled together, it was found that barrier oxide dissolution time can be calculated theoretically by using experimental data obtained from anodization experiments conducted under the same condition for different durations remaining in Stage 3. Table 4.2 and Figure 4.51 show the experimental data and FESEM images of obtained nanotubes anodized (at 25 °C) for different durations remaining in Stage 3. The chemical shortening rate (CSR) related to the chemical dissolution of the nanotubes can be calculated with equation 4.2. This equation was produced based on the determination of the shortened (dissolved) nanotube thickness during Stage 3 using the difference between calculated thickness (assuming there is no chemical shortening) and the actual thickness of 2 samples. The chemical shortening rate of the tubes was determined by dividing shortened nanotube thickness by elapsed time. In equation 4.2, CSR is the chemical shortening rate of the nanotubes ($\mu\text{m min}^{-1}$), Q_2 and Q_1 are the total charge consumed per cm^2 during anodization for two different time durations (C cm^{-2}), GR is the field-assisted growth rate which is obtained experimentally by anodization remaining in Stage 1 ($\sim 0.7 \mu\text{m C}^{-1} \text{cm}^2$), L_2 and L_1 are the respective final length of nanotubes (μm) for two different anodization durations, t_2 and t_1 are the related anodization durations (min).

$$CSR = \frac{[(Q_2 - Q_1) \cdot GR] - (L_2 - L_1)}{t_2 - t_1} \quad (4.2)$$

When the chemical shortening rate of the tubes is known for a particular anodization condition, the dissolution time of the protective top barrier oxide under the same condition can be calculated in accordance with equation 4.3:

$$BDT = t - \frac{(Q \cdot GR) - L}{CSR} \quad (4.3)$$

In this equation, BDT is the initial barrier oxide dissolution time (min), t is the anodization duration (min), Q is the total charge consumed per cm^2 during anodization (C cm^{-2}), GR is the field-assisted growth rate which is obtained experimentally by anodization remaining in Stage 1 ($\mu\text{m C}^{-1} \text{cm}^2$), L is the final length of nanotubes (μm), CSR is the shortening rate of the nanotubes at the top ($\mu\text{m min}^{-1}$).

Table 4.3 shows the chemical shortening rate (CSR) and barrier oxide dissolution time (BDT) calculated for the samples anodized at 25 °C. The shortening rate of the tubes at 25 °C was calculated using equation 4.2, and the average value of 19.4 nm min⁻¹ was obtained. By using calculated chemical shortening rate, barrier oxide dissolution time at 25 °C was calculated using equation 4.3; and 130.1 minutes was obtained for the complete dissolution of initial barrier oxide, which is in accordance with experimental data (Figure 4.50(a), (b) and (c)).

Table 4.3 : Chemical shortening rate (CSR), barrier oxide dissolution time (BDT), and rate constants of the samples anodized at 25 °C and 5 °C were obtained by comparing samples anodized for different durations (Equation 4.2 and equation 4.3).

Anodization Temperature (°C)	Anodization durations of compared samples	Chemical shortening rate of the nanotubes (CSR) (nm min ⁻¹)	Initial Barrier Oxide Dissolution time (BDT) (min)	BDT (Average of 3 calculations) (min)	1/BDT Rate constant (Average) (k) (min ⁻¹)
25	240 – 390 (min)	19.25	128.5	130.1	7.686 x 10 ⁻³
	240 – 540 (min)	19.40	129.4		
	390 – 540 (min)	19.55	132.5		
5	660 – 1020 (min)	6.28	419.7	414.1	2.415 x 10 ⁻³
	660 – 1440 (min)	6.20	416.8		
	1020 – 1440 (min)	6.14	405.8		

In conclusion, for samples anodized at 25 °C (in conditions stated in the experimental part); nanotubes started and continued to grow with a rate of ~0.7 µm C⁻¹ cm² for approximately 130 minutes (Stage 1); subsequently, nanopore/nanotube transition occurred, and open tube top ordered nanotubes were observed (Stage 2); and after 130 minutes, nanotube film continued to grow with the same rate (~0.7 µm C⁻¹ cm²) but simultaneously shortened with a rate of ~19.4 nm min⁻¹ until the end of anodization (Stage 3).

4.2.4 Extrapolation of the model

As demonstrated in the previous sections, it is possible to determine the morphology and film thickness of titania nanotube film during anodization under a particular

condition by using the defined model based on understanding the kinetics of different stages of the growth process. In this model, the initial barrier oxide dissolution rate is the critical parameter for determining the transition time from Stage 1 to Stage 3. As the initial barrier oxide dissolution is a chemical process, its activation energy can be calculated using the Arrhenius equation, and the barrier oxide dissolution rates at different temperatures can be derived.

To determine the activation energy of the process, another set of experiments was conducted at 5 °C. In this set of experiments, the same procedure was repeated; the field-assisted growth rate was determined by anodization experiments remaining in Stage 1, and the shortening rate of the nanotubes was determined by anodization experiments remaining in Stage 3. Table 4.2 shows the experimental results for samples anodized at 5 °C. As shown in Figure 4.52, while the nanotube film thickness increased during the anodization performed at 5 °C, the barrier oxide layer on the surface weakened due to chemical dissolution in accordance with Stage 1 of the model. Also, the extension of anodization duration resulted in an increase in nanotube film thickness along with the formation and progression of the nanograin layer (Figure 4.53).

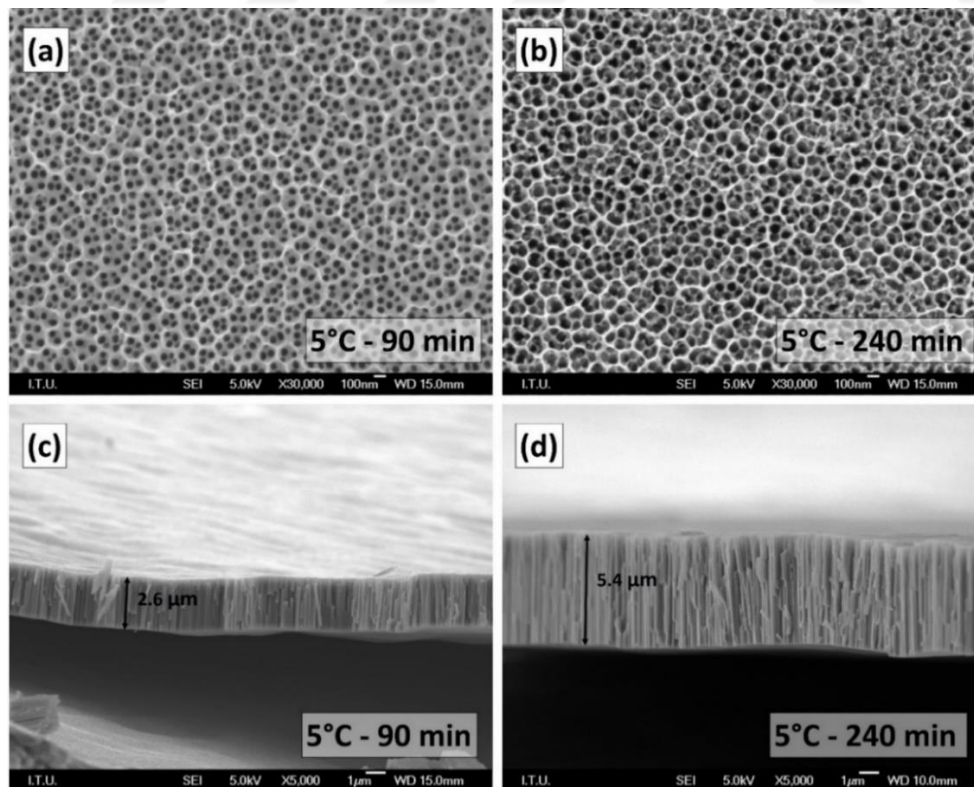


Figure 4.52 : FESEM images top view of (a) 90 min, (b) 240 min; cross-sectional view of (c) 90 min, (d) 240 min anodized samples at 5 °C.

Field-assisted growth rate (per coulomb) in Stage 1 at 5 °C was determined as $\sim 0.7 \mu\text{m C}^{-1} \text{cm}^2$, equivalent to the samples anodized at 25 °C. Then, the shortening rate of the tubes and barrier oxide dissolution time for 5 °C was calculated as $\sim 6.2 \text{ nm min}^{-1}$ and 414.1 minutes by using equation 4.2 and equations 4.3, respectively (Table 4.3).

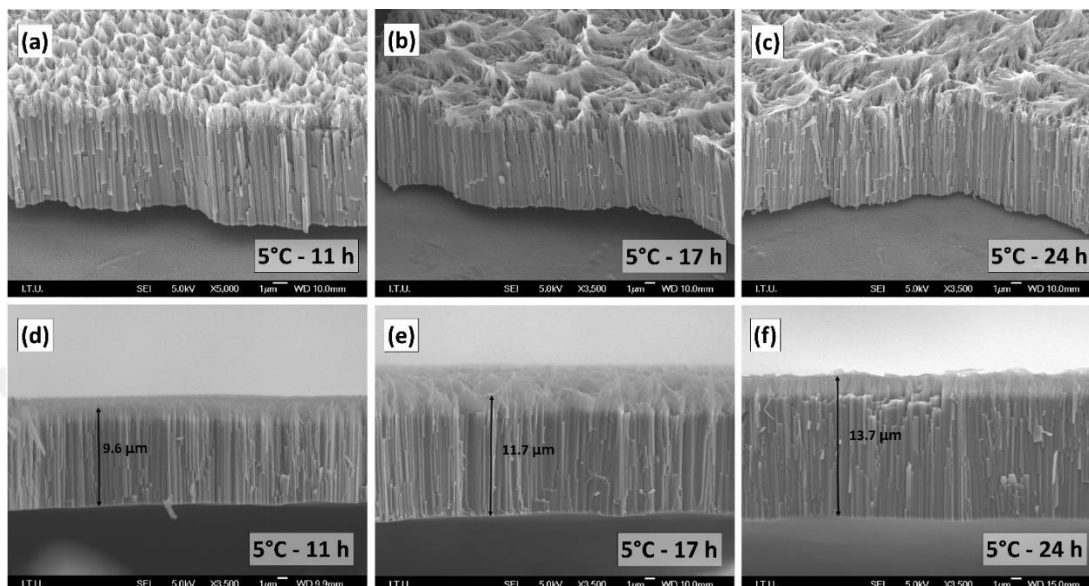


Figure 4.53 : FESEM images showing morphology and thickness of the samples anodized at 5 °C for (a), (d) 11h; (b), (e) 17h; (c), (f) 24h in Stage 3. The final thickness of the TiO₂ nanotube films is shown in the cross-sectional view.

Calculated barrier oxide dissolution times (for 25 °C and 5 °C) were tested for consistency by conducting anodization experiments for 130 min at 25 °C and 415 min at 5 °C before being used in activation energy calculations.

As can be observed from Figure 4.54, calculated times for BDT are in accordance with the calculations. Additionally, the field-assisted growth rates (per coulomb) of the nanotubes that were calculated using total charge and final thickness data (Table 3) are in accordance with the growth rate during Stage 1 (0.683 and $0.691 \mu\text{m C}^{-1} \text{cm}^2$ for 25 °C and 5 °C respectively). Obtained growth rate values are very close to $0.7 \mu\text{m C}^{-1} \text{cm}^2$, which shows that nanograss formation and the shortening of the tubes started very recently for both anodization temperatures and calculated durations. As the calculated values are consistent with the experimental values, the activation energy for the barrier oxide dissolution process can be calculated using 25 °C and 5 °C anodization data.

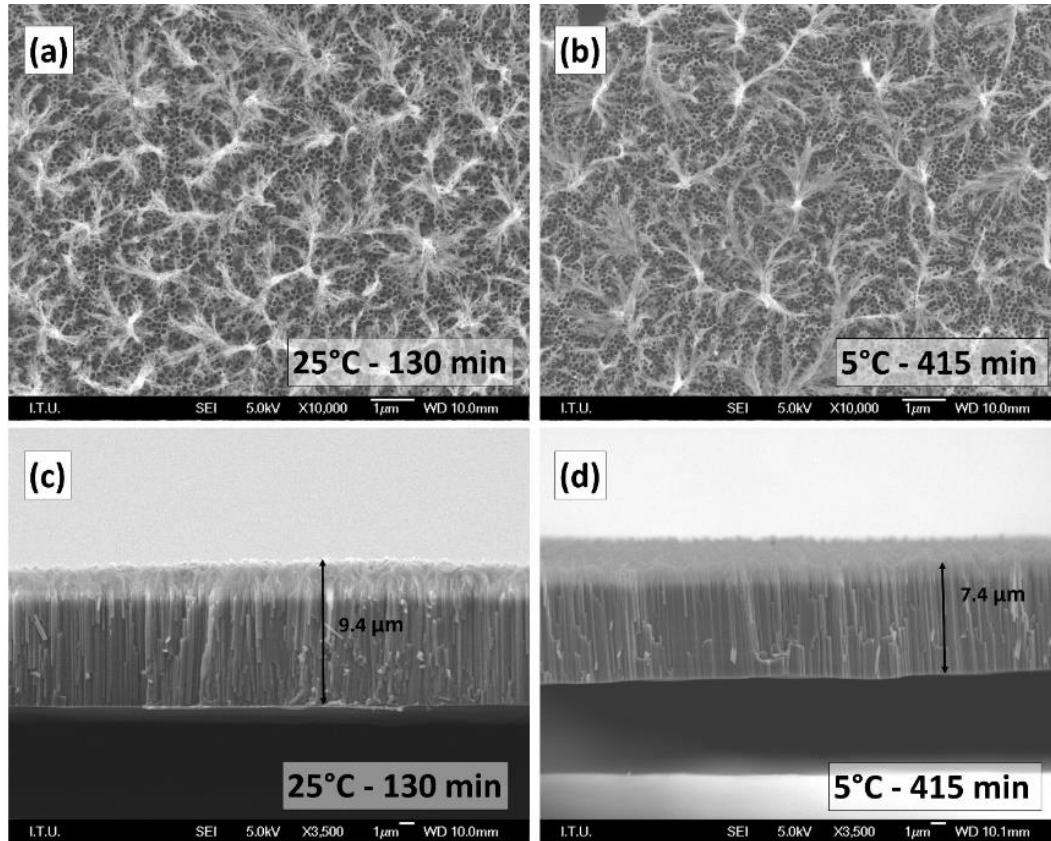


Figure 4.54 : FESEM images showing morphology and thickness of the samples anodized at (a), (c) 25 °C for 130 min; (b), (d) 5 °C for 415 min for durations corresponding to BDT. The final thickness of the TiO₂ nanotube films is shown in the cross-sectional view.

Dissolution time of initial barrier oxide (BDT) can be simply defined as the division of initial barrier layer thickness by dissolution rate of this layer. Barrier oxide thickness is known to be exponentially dependent on temperature and can be represented by an Arrhenius-type equation, as the plot of $\ln$ function of anodizing ratio data versus T^{-1} gives a straight line of slope [15]. On the other hand, it is well-known that many of the reactions in solution obeys the Arrhenius law and have activation energy depending on the reaction type and medium conditions. The rate constant of most solution reactions, which show Arrhenius behavior, increases roughly 2-4 times per 10°C increase on the temperature, depending on the activation energy value [98]. Chemical dissolution kinetics of the TiO₂ particles in aqueous HF-HCl solutions was studied in an early work, and it was shown that the chemical dissolution rate of TiO₂ is exponentially dependent on the temperature and fits well with the Arrhenius equation [99]. Since temperature dependence of both the barrier oxide thickness and chemical dissolution rate of this layer can be represented by Arrhenius-type relations, undoubtedly, the temperature dependence of barrier oxide dissolution time (BDT) can

be represented by Arrhenius-type relation ($e^A/e^B=e^{A-B}$) [98]. Therefore, in this study, $1/\text{BDT}$ (min^{-1}) was used as a rate constant to determine the temperature dependence of the barrier oxide dissolution process. The activation energy of the process was determined by using 5°C and 25°C anodization data (Table 4.4) according to equation 4.4:

$$E_a = \ln \frac{k_2}{k_1} \times \frac{R(T_1 T_2)}{(T_2 - T_1)} \quad (4.4)$$

In this equation, E_a is the activation energy for barrier oxide dissolution (cal mol^{-1}), k is the rate constants of the dissolution (BDT^{-1} (min^{-1})) for 5 and 25°C , R is the gas constant ($1.987 \text{ cal mol}^{-1} \text{ K}^{-1}$), T is the anodization temperature (K). Accordingly, an activation energy equivalent to $9.53 \text{ kcal mol}^{-1}$ was obtained (Figure 455).

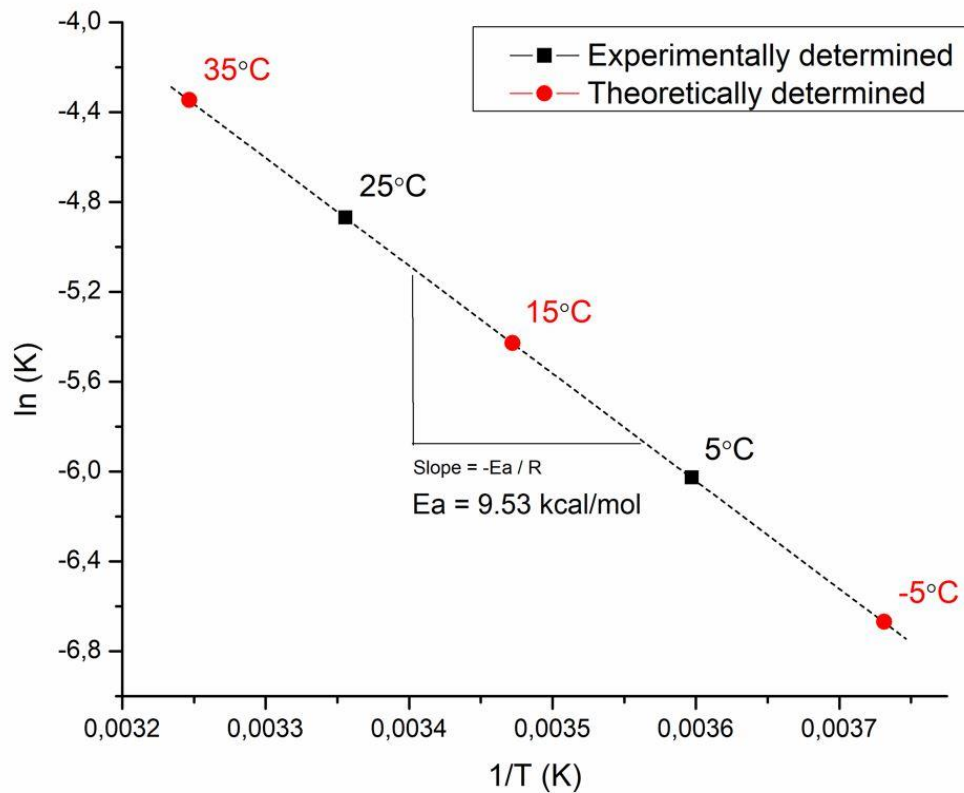


Figure 4.55 : $\ln k$ (rate constant "k" is $1/\text{BDT}$ in this work) versus inverse temperature plot to determine the activation energy for barrier oxide dissolution process. Rate constants for 25°C and 5°C were obtained experimentally. The rate constant for different temperatures (35°C , 15°C , -5°C) is derived theoretically using the activation energy and Arrhenius equation.

Dissolution BDT^{-1} values for three different temperatures (35°C , 15°C , and -5°C) were determined by using calculated activation energy and employing the Arrhenius equation:

$$k = A \times e^{-\frac{E_a}{RT}} \quad (4.5)$$

In this equation, k is the rate constant of the dissolution ($\text{BDT}^{-1} (\text{min}^{-1})$), E_a is the activation energy for barrier oxide dissolution (cal mol^{-1}), R is the gas constant ($1.987 \text{ cal mol}^{-1} \text{ K}^{-1}$), T is the anodization temperature (K). Calculated initial barrier oxide dissolution times and derived values verified experimentally at corresponding temperatures (35°C , 15°C , and -5°C) are presented in Table 4.4.

Table 4.4 : Calculated barrier oxide dissolution time (BDT) for different temperatures (35°C , 15°C , -5°C) using activation energy and the Arrhenius equation. In the table, experimental data for 25 and 5 C are also included.

Anodization Temperature ($^\circ\text{C}$)	Determination method	1/BDT Rate constant (k) (min^{-1})	BDT (min)	Total Charge Density (Q) (C cm^{-2})	Final Nanotube Length (L) (μm)	Growth Rate of Tubes (GR) ($\mu\text{m C}^{-1} \text{ cm}^2$)
35	Calculation	12.961×10^{-3}	77.2	15.66	$10.4 (\pm 0.3)$	$0.664 (\pm 0.019)$
25	Experimental	7.686×10^{-3}	130.1	13.76	$9.4 (\pm 0.3)$	$0.683 (\pm 0.022)$
15	Calculation	4.396×10^{-3}	227.5	12.07	$8.2 (\pm 0.2)$	$0.679 (\pm 0.017)$
5	Experimental	2.415×10^{-3}	414.1	10.71	$7.4 (\pm 0.2)$	$0.691 (\pm 0.019)$
-5	Calculation	1.269×10^{-3}	788.2	9.77	$6.8 (\pm 0.2)$	$0.696 (\pm 0.020)$

In Figure 4.56 and Figure 4.57, FESEM images and time-dependent current density transient of samples anodized at 35°C , 15°C , and -5°C for calculated durations corresponding to complete initial barrier oxide dissolution are given. As all three samples were obtained without barrier oxide residue on the surface, calculated BDT data is consistent with the experimentally obtained results (Figure 4.56(a), (b), and (c)). Growth rates (per coulomb) of 0.664 , 0.679 , $0.696 \mu\text{m C}^{-1} \text{ cm}^2$ were obtained for 35°C , 15°C and -5°C , respectively. The growth rates for 15°C and -5°C were very close to the expected value of $0.7 \mu\text{m C}^{-1} \text{ cm}^2$, which shows that nanoglass formation and the shortening of the tubes started very recently. For the sample anodized at 35°C , the growth rate value ($0.664 \mu\text{m C}^{-1} \text{ cm}^2$) was slightly lower than the expected value of $0.7 \mu\text{m C}^{-1} \text{ cm}^2$, and the early phase of nanoglass formation was seen on the sample (Figure 4.56(a)). This result can be attributed to the faster dissolution rate of the top barrier layer at high temperatures, making it more difficult to determine the precise time for this dissolution.

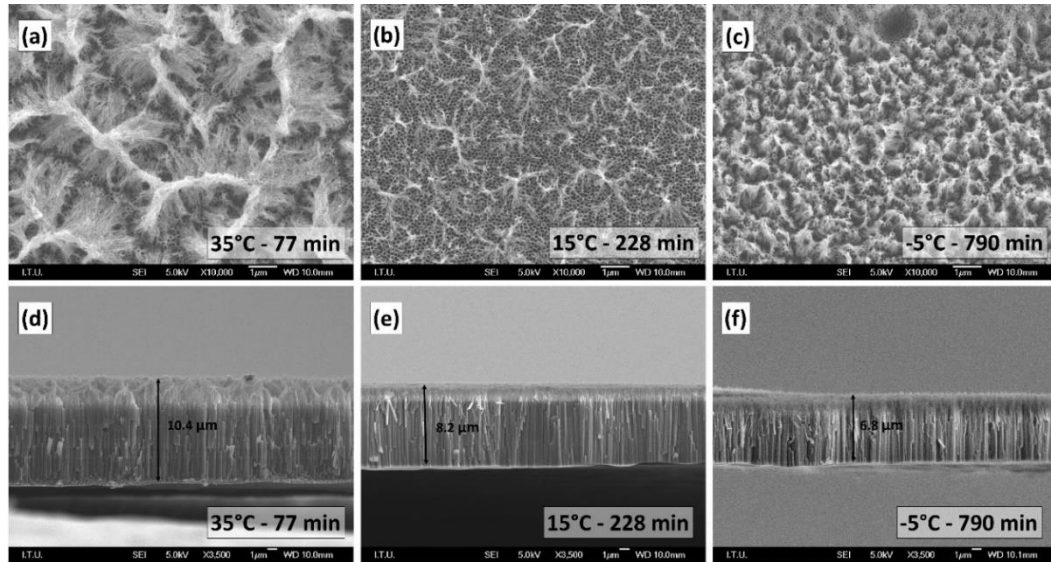


Figure 4.56 : FESEM images showing morphology and thickness of the samples anodized at (a), (d) 35 °C for 77 min; (b), (e) 15 °C for 228 min; (c), (f) -5 °C for 790 min. (Durations corresponding to calculated BDT). The final thickness of the TiO₂ nanotube films is shown in the cross-sectional view.

These experiments and calculations verified that temperature dependence of the barrier oxide dissolution time (BDT) shows Arrhenius-like behavior, and BDT values for different anodization temperatures can be calculated using the activation energy of the process. Considering that BDT indicates the time-stamp at which morphological transformation occurs, and the growth mode completely changes during anodization, the control over the anodization process increases significantly with the verified model. Hence, it becomes possible to obtain nanotubes in the desired morphology, one of the most critical challenges in anodization studies, by anodization conducted at theoretically derived parameters.

Another remarkable finding of the study is the possibility of determining the anodic oxide thickness free from barrier oxide residue or nanograss at different anodization temperatures, as the plot of nanotube thickness that corresponds to BDT at different temperatures indicated a linear relation between them (Figure 4.58). For the modeled condition; it was shown that open-top nanotubes ranging from 6.8 μm to 10.4 μm could be obtained by tuning anodization temperature (-5 °C to 35 °C) and anodization duration according to the model. Thus, while obtaining controlled nanotube film thickness, disadvantages caused by barrier oxide residue or nanograss can be avoided. Besides, different morphologies that may be needed in different studies (i.e., barrier top or nanograss top) with controlled thickness can also be obtained. It becomes

possible to precisely control the morphology and thickness of the titania nanotube film during anodization by using the proposed approach.

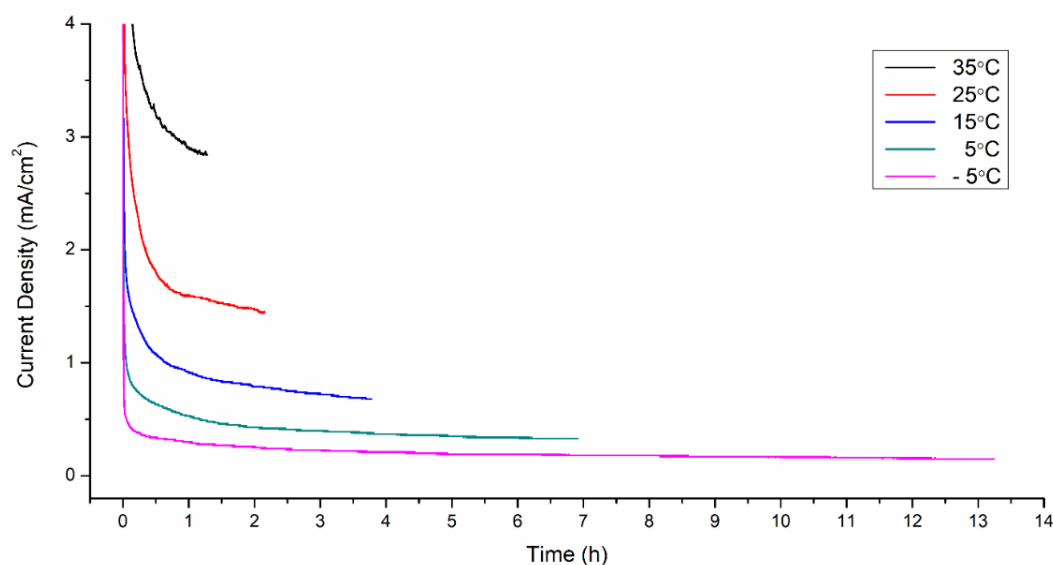


Figure 4.57 : Time-dependent current density transients recorded at 50V during anodization of the samples for durations corresponding to BDT. 35 °C – 77 min, 25 °C – 130 min, 15 °C – 228min, 5 °C – 415 min, -5 °C – 790 min in 0.3 wt% NH₄F, 1 vol% H₂O (EG).

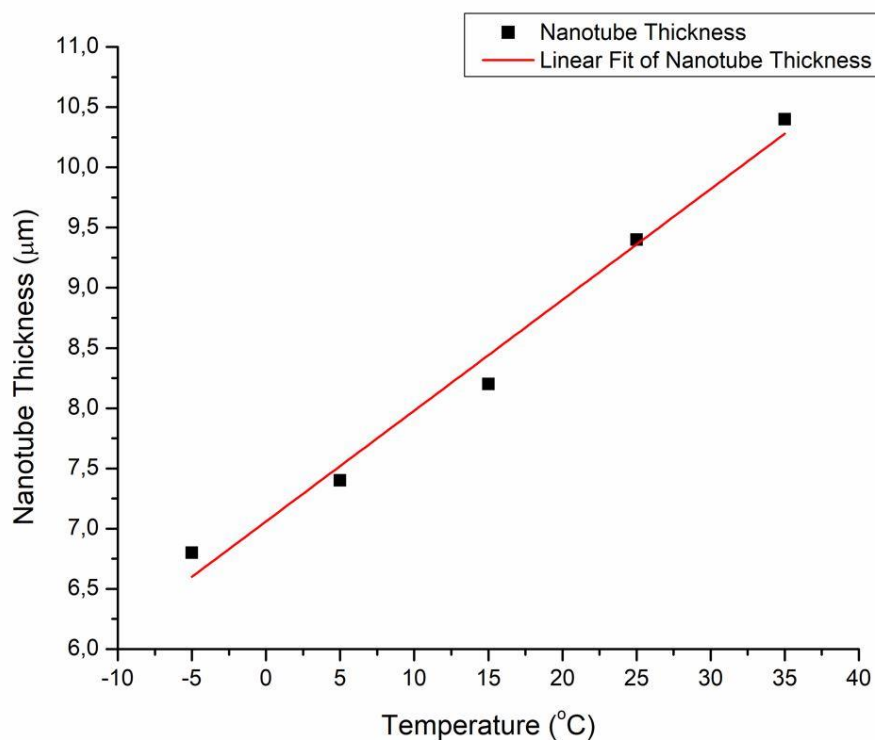


Figure 4.58 : Final nanotube film thickness (open tube top) obtained by anodization of the samples for durations corresponding to BDT. 35 °C – 77 min, 25 °C – 130 min, 15 °C – 228min, 5 °C – 415 min, -5 °C – 790 min in 0.3 wt% NH₄F, 1 vol% H₂O (EG).

The proposed model is also applicable to other anodization conditions conducted in ethylene glycol-based electrolytes and aims to combine the growth kinetics with the final morphologies. Thus, by conducting six experiments (minimum) in an electrolyte with a different composition or under different anodization conditions (voltage, stirring type, stirring rate, etc.), one can identify the conditions for obtaining different morphologies with controlled thickness. Thus, the developed model offers a method for characterizing a working condition and controlling it to obtain the desired titania nanotube morphology and length.

We showed that even under a given set of experimental conditions (using one voltage, one electrolyte composition, one electrolyte stirring rate, etc.), it was possible to obtain open-top nanotubes (without barrier oxide residue or nanograin) ranging from 6.8 μm to 10.4 μm in a controlled way by tuning anodization temperature and duration. By changing the electrolyte composition and anodization parameters and characterizing the new conditions with this model, different nanotube length ranges (wider or narrower ranges) can be obtained.



5. CONCLUSIONS

Within this study, growth kinetics and morphology transitions during porous titanium anodization in ethylene glycol-based electrolytes are investigated. The results of this study indicate the possibility of tuning the morphology of nanostructures formed during the anodization of titanium by using a developed kinetic model. For constructing this kinetic model, the effects of experimental parameters on nanotube growth and morphology were first investigated, and parameters were optimized for reproducible results.

Moisture absorption of the anodization electrolyte was eliminated, and reproducibility of the anodization was ensured by conducting all solution preparations and anodization operations inside a glovebox. The anodization parameters were investigated and optimized in ethylene glycol-based electrolytes containing 0.6 wt % NH_4F , 1 vol % H_2O . A two-step anodization procedure using 50 V anodization voltage at 30 °C for 180 min improved the pre-anodization surface roughness. 750 rpm stirring rate (using a 2 cm magnetic bar) provided effective temperature control during anodization. Anodic current decreased as expected during repeated anodization operations in the same electrolyte because of the consumption of free fluoride ions. Interestingly, after keeping the electrolyte unused overnight, the anodization current recovered to its initial value giving the same morphological surface features. These results indicated that the recovery of free fluoride ions during waiting is highly probably because of the decomposition of $[\text{TiF}_6]^{2-}$ complexes into TiF_3 , resulting in free fluoride release.

It was demonstrated that process temperature has a dominant effect on the chemical dissolution of the anodic oxide. Three different morphologies were obtained during anodization experiments performed at 50 V and 30 °C for different durations (5 min to 40 min). For 5 min and 10 min anodized samples, compact barrier oxide morphology, for 20 min anodized sample open-top nanotube morphology, and 40 min anodized sample nanograss morphology was obtained. It was deduced that the surface morphology progresses in the order of barrier layer, open nanotubes, and nanograss structure, indicating the progressive nature of the process.

In the light of experimental results, a growth model based on the initial barrier oxide dissolution has been proposed, and experimental studies were realized to validate the model. Accordingly, we divided the growth process into three stages (I. Growth under initial barrier layer, II. Nanopore to nanotube transition, III. Nanoglass formation) and evaluated the anodization stage-dependent tube growth kinetics. The growth rate of the oxide layer beneath the initial barrier layer is controlled by the field-assisted growth as long as the top barrier layer persists (Stage 1). Thus, to determine the growth rate, anodization experiments were conducted at different temperatures (for 25 °C and 5 °C) for different durations remaining in stage 1; using 50 V anodization voltage in ethylene glycol-based electrolytes that contain 0.3 wt % NH_4F , 1 vol % H_2O . The field-assisted growth rate of $\sim 0.7 \mu\text{m C}^{-1} \text{cm}^2$ was obtained independent of the electrolyte temperature and the anodization duration. After the complete dissolution of the initial barrier oxide, nanopore to nanotube transition was observed (Stage 2). Dissolution of the initial barrier layer totally change the growth process of the anodic oxide; in addition to the electrochemical growth of the anodic oxide with the same rate, chemical dissolution starting from the top of the anodic oxide layer also takes place, resulting in the formation of nanoglass and also shortening of the tubes (Stage 3).

Relying on these results, we have demonstrated that the persistence of the top barrier layer is necessary for the growth of the anodic oxide layer in a controlled manner. A kinetic model was developed to determine the persistence time of this top barrier oxide layer. The chemical shortening rate of the nanotubes due to chemical dissolution was determined experimentally (for 25 °C and 5 °C) by using two different anodization durations remaining in stage 3, which allowed us to calculate the barrier oxide dissolution time (BDT). Barrier oxide dissolution times for 25 °C and 5 °C are calculated as 130.1 min and 414.1 min, respectively, and verified experimentally by anodization conducted for the corresponding BDT values. As the dissolution of the top barrier layer is a chemical process, its activation energy was calculated using the experimentally determined parameters that allowed us to determine the temperature dependence of BDT. Additional experiments conducted at 35 °C, 15 °C, and – 5 °C by using the theoretically calculated BDT values verified the model's validity. Besides controlling the final morphology, it is shown that the plot of nanotube thickness that corresponds to BDT at different temperatures indicates a linear relation; and open-top

nanotubes ranging from 6.8 μm to 10.4 μm can be obtained by tuning anodization temperature and duration according to this model.

This approach gives the opportunity to tailor titania nanotube thickness (within a specific range) and desired nanotube morphology (barrier top, open tube-top, or nanograss) by tuning anodization temperature and duration according to the proposed model. As further work, this model approach can be applied to different electrolyte compositions and anodization parameters for modeling the growth kinetics of nanotubes under different conditions.





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CURRICULUM VITAE

Name Surname : Eren SEÇKİN

EDUCATION :

- **B.Sc.** : 2007, ITU, Faculty of Chemical and Metallurgy, Metallurgy and Materials Engineering
- **M.Sc.** : 2010, ITU, Institute of Science and Technology, Material Science and Engineering Programme

PROFESSIONAL EXPERIENCE AND REWARDS:

- 2016 – Current : R&D Chief / Researcher
B-PLAS Bursa Plastic Inc.
- 2009 – 2016 : Managing Partner / Researcher
IDEAPORT Innovation Energy and Automation Ltd.
- TUBITAK National Graduate Scholarship for Ph.D. Programme (2010-2015)
- TUBITAK National Graduate Scholarship for Ms.C. Programme (2007-2010)

PUBLICATIONS, PRESENTATIONS AND PATENTS ON THE THESIS:

- **Seckin E.**, Urgan M. 2021. A Kinetic Model for Determining Morphology Transitions and Growth Kinetics of Titania Nanotubes During Anodization of Titanium in Ethylene Glycol Based Electrolytes, *Surface and Coatings Technology*, 409, 126840.

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