

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL

**EFFECT OF ELECTROLYTE AND ELECTRICAL PARAMETERS ON THE
ANODIC OXIDATION OF Ti TO IMPROVE PHOTOCATALYTIC
PERFORMANCE OF TiO₂ NANOTUBE STRUCTURES**



Ph.D. THESIS

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Department of Materials Science and Engineering

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NOVEMBER 2023

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ

**TiO₂ NANOTÜP YAPILARIN FOTOKATALİTİK PERFORMANSINI
ARTIRMAK İÇİN Ti'NİN ANODİK OKSİDASYONU ÜZERİNE ELEKTROLİT
VE ELEKTRİKSEL PARAMETRELERİN ETKİSİ**

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FOREWORD

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Mert ALTAY



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ABBREVIATIONS

CP-Ti	: Commercially Pure Titanium
EDS	: Energy Dispersive Spectrometer
MB	: Methylene Blue
MWCNT	: Multi Walled Carbon Nanotube
PL	: Photoluminescence
Ra	: Mean Surface Roughness
SEM	: Scanning Electron Microscope
TiO₂	: Titanium Dioxide
UV-DRS	: Ultraviolet–Visible Diffuse Reflectance Spectroscopy
XPS	: X-Ray Photoelectron Spectroscopy
XRD	: X-Ray Diffraction



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SUMMARY

TiO₂ is a semiconductor material that, when stimulated by photons with energy sufficient to overcome its band gap (3.0-3.2 eV), generates electron-hole pairs. By interacting with one another or through a succession of redox reactions, these charge carriers eventually have the capacity to mineralize a wide range of organic compounds, including dyes, surfactants, aromatics, and alkanes. This property makes various TiO₂ forms (powder, nanotube, nanorod, etc.) appropriate for a variety of applications in the energy and environmental domains, such as solar cells, hydrogen production, water purification, air purification, and others.

This thesis study was undertaken to investigate production, characterization and photocatalytic performance of TiO₂ nanostructures as a very promising semiconductor photocatalyst. Anodic oxidation process utilized for production of TiO₂ nanostructures from commercially pure titanium foils. Various electrolytes and electrical parameters explored to investigate their effect on the surface preparation. Produced nanostructures characterized by surface morphology analyses with optical and electron microscopy, surface phase and structure analyses with XRD, XRF and Raman, optical properties analyses with photoluminescence and UV-DRS, and with organic contaminant degradation tests.

One of the anodic oxidation parameters studied in the scope the thesis was cyclic bipolar voltage. In this work group different duty cycle and frequency values was experimented and nano structures successfully produced on titanium foils. Results showed that the increasing positive pulse duration, number of successive positive pulses and neutral period of the cycle could increase nanotube diameter. Also, application of negative voltage clearly deteriorated the nanotube morphology and produced a sponge like structure at the surface.

Effect of pre-deformation mode and strain level on the photocatalytic performance of TiO₂ nanotubes produced by anodic oxidation on titanium foils were also investigated. In this study set, three different amounts of tensile and compression strains applied to titanium foil prior to anodic oxidation. Results showed that pre-deformation on titanium foils could have a strong effect on photocatalytic performance of TiO₂ nanotubes produced from these foils. Especially cold rolling deformation was quite successful in improving photocatalytic performance. On the other hand, critical amount of tensile deformation did improve photocatalytic performance, where further deformation amount deteriorated it.

One other anodic oxidation parameter studied in the thesis was effect of carbon structure, namely carbon nanotubes, addition to electrolyte. Different amounts of carbon nanotubes was added to anodic oxidation electrolyte since, in term of improving

photocatalytic performance, carbon is a very effective dopant for TiO₂ structures. Results showed that deposition of carbon structures on TiO₂ nanotubes was successful and photocatalytic performance of these doped samples were better than un-doped ones. However due to clustering and covering up effect of carbon structures, with the increase at the carbon concentration in electrolyte, photocatalytic performance decreased.

Prior to anodic oxidation experiments, a surface preparation method named electropolishing and a surface coating method named hot-dip aluminizing also studied. Electropolishing of titanium foils was experimented to produce smooth surfaces for further processes. Successfully electropolished titanium surfaces were prepared after trials with various process parameters and these surfaces used in anodic oxidation trials. Aluminizing of titanium foils were investigated to produce intermetallic surfaces for further processes/applications. Intermetallics of aluminum and titanium successfully produced with this method and these structures greatly improved high temperature oxidation resistance of titanium foils. Anodic oxidation of these surfaces was not undertaken in the scope of this thesis, however formation of nanostructures on intermetallics could be a very interesting further study.

As a whole, thesis study investigated electropolishing, aluminizing and anodic oxidation of titanium foils. Successful parameters for electropolishing of commercially pure titanium was established. Additionally, various ways to improve photocatalytic performance of a TiO₂ nanostructures demonstrated. In this context, outputs of the thesis study could be useful in two very strategically important and urgent fields namely, energy and environment.

TiO₂ NANOTÜP YAPILARIN FOTOKATALİTİK PERFORMANSINI ARTIRMAK İÇİN Ti'NİN ANODİK OKSİDASYONU ÜZERİNE ELEKTROLİT VE ELEKTRİKSEL PARAMETRELERİN ETKİSİ

ÖZET

Titanyum dioksit, çok yönlü, endüstride ve günlük yaşamda çeşitli uygulamaları olan ve yaygın olarak kullanılan bir malzemedir. Doğal olarak oluşabilen rutil ve anataz gibi fazlara sahip bir bileşik olan titanyum dioksit sentetik olarak da farklı yöntemlerle üretilmektedir.

Titanyum dioksitin en dikkat çekici özelliklerinden biri olağanüstü beyaz rengi ve yüksek opaklığıdır. Bu özellik onu boyalar, mürekkepler ve kozmetikler dahil olmak üzere çok çeşitli uygulamalar için ideal bir pigment yapmaktadır.

Titanyum dioksit aynı zamanda çok önemli bir fotokatalitik yarı iletken malzemedir. Kendi bant aralığı değerini (3.0-3.2 eV) aşmasına yetecek enerjiye sahip fotonlarla uyarıldığında elektron-boşluk ikilileri oluşturur. Bu özelliği sayesinde hava ve su ortamlarında boyalar, sürfektanlar, aromatikler gibi pek çok organik bileşiği parçalama yetisine sahiptir. Bu yeti farklı faz ve morfolojik yapılarda titanyum dioksitin enerji ve çevre uygulama alanlarında değerlendirilmesini sağlar. Bu uygulama alanlarının başlıcaları; güneş pilleri, hidrojen üretimi, su ve hava arıtmadır. Günümüzde yaşanan dünyasal gelişmeler açısından oldukça stratejik konular haline gelen enerji ve çevre sektörü konularında yer alan bir malzeme olması nedeniyle titanyum dioksit'e yönelik araştırma ve geliştirme çalışmaları oldukça önemlidir.

Titanyum dioksit, yarı iletken özellikleri ve ışığı verimli bir şekilde soğurma kabiliyeti nedeniyle boyaya duyarlı güneş pillerinde (DSSC'ler) çok önemli bir bileşen olarak kullanılır. DSSC'ler, güneş ışığını elektrığe dönüştüren düşük maliyetli ve çevre dostu güneş pilleridir. Titanyum dioksitin elektron transferini kolaylaştırma yeteneği ve uzun süre ışığa maruz kaldığında kararlılığı, onu bu amaç için ideal bir malzeme yapmaktadır.

Son yıllarda, ilaç dağıtım sistemleri, kendi kendini temizleyen yüzeyler ve antimikrobiyal kaplamalar dahil olmak üzere çeşitli uygulamalarda titanyum dioksit malzemeler kullanılmaktadır.

Yukarıda belirtilen uygulamaların çoğunluğunda titanyum dioksitin nano boyutlu yapıları tercih edilmektedir. Bu yapılar içerisinde nanoparçacıklar, nanotüpler, nanoçubuklar vb. yapılar yer almaktadır. Bu yapılar oluşturmak için sol-gel, hidrotermal sentez, kimyasal buhar biriktirme, lazer ablasyon ve anodik oksidasyon gibi pek çok farklı yöntem bulunmaktadır.

Bu yöntemler arasında yer alan anodik oksidasyon yöntemi, titanyumun kontrollü oksidasyonu ile titanyum dioksit nanoyapıları, özellikle nanotüpleri üretmek için yaygın olarak kullanılan bir yöntemdir. Anodik oksidasyon işlemi sırasında nanoyapılar organize bir şekilde titanyum yüzeyinde büyütülebilir.

Titanyumun anodik oksidasyon prosesine önemli etkileri olan proses parametreleri vardır. Prosesle en çok etki eden parametreler arasında elektrolit türü, sıcaklığı, anodizasyon voltajı, süresi yer almaktadır. Bunun yanında ön işlemler, yüzey hazırlama, katot seçimi, anot-katot mesafesi, elektrolit karıştırma hızı gibi parametreler de üretilen nanoyapıları farklılaştırabilmektedir.

Genel olarak bakıldığında anodik oksidasyon yöntemi, titanyum dioksit nanoyapıların üretilmesi için çeşitli avantajlar sunmaktadır. Proses, kontrol edilebilir boyutlara ve en boy oranlarına sahip, yüksek düzeyde düzenli, dikey olarak hizalanmış nanotüp dizilerinin oluşumunu mümkün kılmaktadır. Üretilen bu nanoyapılar, fotokataliz, enerji depolama ve biyomedikal cihazlar gibi uygulamalar için faydalı olan yüksek yüzey alanına da sahip olmaktadır. Bunun yanında istenen nano yapı özelliklerini elde etmek için deneysel parametrelerin dikkatli bir şekilde kontrol edilmesi oldukça önemlidir.

Bu tez çalışmasında, titanyum folyolardan anodik oksidasyon yöntemi ile titanyum dioksit nanoyapıların üretilmesi, üretilen nanoyapıların karakterizasyonu ve fotokatalitik özellikleri incelenmiştir. Bu kapsamda farklı elektrolitler, elektriksel parametreler kullanılarak üretilen yüzeye etkileri araştırılmıştır. Üretilen nanoyapıların morfolojisi optik ve elektron mikroskopları ile, faz ve bileşik yapıları XRD, XRF ve Raman analizleri ile, optik özellikleri fotoluminesans ve UV-DRS yöntemleri ile ve fotokatalitik performansları organik bileşenlerin parçalanması deneyleri ile karakterize edilmiştir.

Tez çalışması kapsamında incelenen bir anodik oksidasyon parametresi periyodik bipolar voltajın etkisidir. Bu çalışmada farklı frekans, iş döngüsü ve voltaj değerleri kullanılarak nanoyapılar üretilmiştir. Üretilen nanoyapıların morfolojilerinin proses parametrelerine göre önemli farklar gösterdiği tespit edilmiştir. Elde edilen sonuçlara göre pozitif voltaj süresinin, pozitif voltaj sıklığının ve nötr voltaj periyodunun artırılması ile anodik oksidasyon ile üretilen titanyum dioksit nanoyapıların çapları büyütülebilmektedir. Bunun yanında elektrokimyasal hücrede titanyum folyolara negatif voltaj uygulanmasının nanotüp morfolojisini bozduğu ve titanyum yüzeyinde nano boşluklar içeren süngerimsi yapılar oluşturduğu tespit edilmiştir.

Araştırılan bir diğer konu da, ön deformasyon işleminin anodik oksidasyon prosesine ve prosesle üretilen nanoyapıların özelliklerine etkisidir. Bu çalışmada titanyum folyolara anodik oksidasyon işlemi öncesinde yüzey yapısının farklılaştırılması amacıyla deformasyon uygulanmıştır. Çekme ve hadde olmak üzere iki farklı deformasyon modu uygulanmış olup her iki mod için de üçer farklı şekil değiştirme oranı kullanılmıştır. Yapılan karakterizasyon analizleri ve fotokatalitik testlerin sonuçlarına göre titanyum folyoların ön deformasyonunun, folyolar üzerinde üretilen titanyum dioksit nanotüplerin fotokatalitik özelliklerine önemli etkileri olduğu tespit edilmiştir. Özellikle hadde deformasyonunun, basma yönünde oluşturduğu gerilimler ile yüzey düzlem yapısını farklılaştırdığı ve bu sayede titanyum dioksit nanotüp yapılarının düzenliliğini arttırdığı belirlenmiştir. Bu değişimler ile nanotüplerin fotokatalitik özellikleri iyileştirilerek organik bileşikler parçalama özellikleri geliştirilmiştir. Çekme deformasyonunun ise yüzey düzlem yapısına önemli bir etkisi olmamıştır. Buna rağmen tane boyutlarını küçültmesi nedeniyle belirli bir orana kadar çekme deformasyonu da titanyum dioksit nanoyapıların fotokatalitik özelliklerini iyileştirmiştir. Fakat, belirli bir değerin üstünde çekme deformasyonu titanyum dioksit nanotüp yapısında önemli bozulmalara sebep olmuştur ve bu durum yüzeyin fotokatalitik özelliklerine de olumsuz yansımıştır.

Tez çalışması kapsamında incelenen bir diğer anodik oksidasyon parametresi de elektrolite yapılan karbon temelli malzeme ilavelerinin proses ve üretilen nanoyapılara etkisidir. Karbon temelli malzemeler olarak çok duvarlı karbon nanotüpler kullanılmıştır. Bu malzemeler anodik oksidasyon elektrolit çözeltisine üçer farklı oranda ilave edilerek anodik oksidasyon testleri yürütülmüştür. Karbonun titanyum dioksit malzemelerin fotokatalitik özelliklerinin geliştirilmesi için oldukça verimli bir katkı maddesi olduğu bilinmektedir. Yapılan karakterizasyon çalışmaları ve fotokatalitik testlerde de bu durum gözlenmiş olup üretilen karbon-titanyum dioksit nanotüp kompozit yüzeylerin, sade titanyum dioksit nanotüp yüzeylere göre daha iyi fotokatalitik özellik gösterdiği belirlenmiştir. Literatüre ilave olarak titanyum dioksit nanotüp-çok duvarlı karbon nanotüp oluşturulmasına yönelik hızlı ve çabuk bir yöntem sunulmuştur. Her ne kadar belirli bir oranda karbon malzeme ilavesinin olumlu etkileri tespit edilmiş olsa da bu oranının üzerinde ilavenin titanyum dioksit nanotüp yüzeylerde topaklanma ve yüzeyi kaplama özelliği nedeniyle optik özellikleri ve dolayısıyla fotokatalitik özellikleri kötüleştirebileceği de tespit edilmiştir.

Tez kapsamında yapılan anodik oksidasyon denemelerine ilaveten, bir titanyum yüzey hazırlama yöntemi olan elektroparlatma ve bir titanyum yüzey kaplama prosesi olan sıcak daldırma aluminyumlama yöntemleri de çalışılmıştır. Elektroparlatma prosesi titanyum folyoların yüzeyin sonraki prosesler için pürüzsüzleştirilmesi amacıyla çalışılmıştır. Farklı elektrokimyasal voltaj, süre ve sıcaklık gibi parametreler kullanılarak deneyler yapılmış olup ideal bir proses parametresi belirlenerek başarılı elektroparlatma işlemleri yapılabilmiştir. Titanyum folyolar elektroparlatma yöntemi ile parlatılarak anodik oksidasyon deneylerinde kullanılmıştır. Aluminyumlama yöntemi ile titanyum folyalar yüzeyinde farklı uygulamalar ve sonraki proseslerde kullanmak amacıyla intermetalikler oluşturulması hedeflenmiştir. Farklı sıcaklık ve süreler denenerek yapılan deneyler sonunda titanyum folyolar yüzeyinde aluminyum-titanyum intermetalikleri başarılı bir şekilde oluşturulmuştur. Oluşturulan bu yüzeylerin titanyumun yüksek sıcaklık oksidasyon direncini önemli oranda arttırdığı belirlenmiştir. Bu yüzeylerin anodik oksidasyonu tez kapsamında çalışılmamış olmasına rağmen, intermetalik yapılardan nanoyapılar üretilmesi ilerisi için oldukça önemli olabilecek bir konu olarak belirlenmiştir.

Genel olarak bakıldığında tez çalışmasında titanyum folyoların elektroparlatılması, sıcak daldırma aluminyumlanması ve anodik oksidasyonu konuları incelenmiştir. Mekanik olarak parlatılması oldukça zorlu olan titanyum folyolarının elektroparlatılmasına yönelik başarılı bir yöntem geliştirilmiştir. Bunun yanında titanyum folyoların anodik oksidasyonu ile üretilen titanyum dioksit nanoyapıların fotokatalitik performanslarının geliştirilmesi için farklı yöntemler sunulmuştur. Bu açıdan tez çalışması çıktılarının günümüzde oldukça önemli ve güncel olan çevre ve enerji teknolojileri alanlarında fayda sağlayabileceği düşünülmektedir.



1. INTRODUCTION

Titanium, a versatile and lightweight metal, has attracted great interest from many industries due to its great mechanical strength and superior corrosion resistance [1]. As the demand for improved surface functions and improved performance of titanium-based materials continues to grow, researchers have shifted their attention to cutting-edge surface engineering approaches. Anodic oxidation, which stands out among these processes, has the potential to improve photocatalytic performance while increasing corrosion resistance by creating nanotube structures on the titanium surface [2,3].

An electrochemical process called anodic oxidation, also known as anodizing or electrochemical oxidation, involves the controlled formation of an oxide layer on the surface of a metal substrate. The development of highly organized nanotube arrays with specific properties is possible with this procedure. These nanotubes have exceptional surface area-to-volume ratios, tunable pore diameters, and high aspect ratios; This makes them special and arouses great interest in various uses such as energy storage, catalysis, sensing and most importantly, photocatalysis [4,5].

An oxide layer grows on the surface of the titanium substrate when exposed to an electrolyte solution and a suitable voltage or current density during the anodic oxidation process. Nanotubes produced can be precisely designed by adjusting anodization parameters such as electrolyte composition, voltage, current density and time. Anodic oxidation is a preferred method for customized surface engineering due to its ability to control nanotube properties such as length, diameter, and wall thickness. This also creates new opportunities for improving the photocatalytic performance of titanium-based materials [6,7].

A potent instrument for environmental cleanup, energy conversion, and sustainable synthesis is photocatalysis, the process by which light energy is used to start chemical processes. Due to its high stability and low toxicity, TiO_2 , a common photocatalyst, is a great choice for a variety of photocatalytic applications. TiO_2 's photocatalytic performance, however, can be greatly enhanced by altering its surface characteristics.

TiO₂ nanotubes' surface morphology, crystal structure, and surface chemistry may all be precisely engineered through the anodic oxidation of titanium, which will also increase their photocatalytic activity [8–10].

The goal of this thesis is to thoroughly explore titanium anodic oxidation and its potential for producing nanotubes, with an emphasis on improving photocatalytic performance. This study aims to provide a thorough knowledge of the fundamental principles underlying the anodic oxidation process and the ensuing nanotube structures by a thorough review of the current literature and experimental analysis. Additionally, this study will look at how different process variables affect the photocatalytic abilities of TiO₂ nanotubes and assess how effective they are in photocatalytic applications.

The findings of this study will expand titanium surface engineering techniques and open the door to the creation of customized nanotube-based materials with improved photocatalytic performance. This study intends to give useful insights for building effective anodic oxidation processes and optimizing nanotube architectures to obtain superior photocatalytic activity by clarifying the underlying mechanisms, assessing the effects of process parameters, and investigating potential applications.

1.1 Properties of Titanium and Its Alloys

1.1.1 General information, extraction and crystal structure

It is commonly recognized that titanium offers qualities that make it appealing to the many industries, but that its limited applications result from its high cost. These industries drawn to titanium's principal qualities, which include its exceptional strength to weight ratio, corrosion resistance, composite compatibility, ballistic properties and low modules. Titanium-based designs frequently result in more dependable, cost-effective, and long-lasting systems and components. Given its benefits, titanium is clearly desirable in a variety of military, civilian, and medical applications [11,12]. Some of the physical properties of titanium is given in Table 1.1 [1].

Table 1.1 : Physical properties polycrystalline α titanium (25°C) [1].

Lattice structure	Close packed hexagonal (HCP)
Space group	P6 ₃ /mmc
B-transition temperature	882 °C
Lattice parameters	a = 0.295 nm c = 0.468 nm c/a = 0.468 nm
Thermal expansion coefficient	8.36 x 10 ⁻⁶ K ⁻¹
Thermal conductivity	14.99 W/mK
Elastic modulus	115 GPa
Shear modulus	44 GPa
Melting point	1668 °C
Boiling point	3287 °C
Density	4.51 g/cm ³

Titanium components frequently outperform expectations in terms of performance and service life while costing less overall. Titanium ranks fourth among iron, aluminium, and magnesium, and ninth among all elements in the earth's crust, with less than 1%. However, this abundance is somewhat illusory in that titanium is not commonly found in economically extractable concentrations. The minerals ilmenite, titanomagnetite, rutile, anatase, and brookite are concentrated sources of the metal. Higher than 90% of titanium is used as oxide in the paint industry and can be encountered in daily life products such as toothpaste, sun screen cream, wall paints. The Kroll process invented at 1930's, which includes reducing TiCl₄ by magnesium, is the most used method for producing titanium. Energy needed to produce a ton of titanium is 16 times higher than the energy needed to produce a ton of steel [11,13].

Pure titanium and most of its alloys at low temperature called α titanium and crystallize in HCP structure. Above 882 °C α titanium shows allotropic transformation and body-centered cubic structure (BCC) called β titanium becomes stable [1].

1.1.2 Alloys and their classification

Through the selective addition of alloying elements to titanium, a wide range of mechanical and physical properties can be obtained. Alloying elements of titanium are classified into three groups named neutral, whose have minimal effect on α - β transition temperature, α stabilizers, whose extent α region to higher temperatures and β stabilizers, whose extent β region to lower temperatures. Table 1.2 shows the notable alloying elements and their classification [13].

Table 1.2. Notable alloying elements and their classification [13].

α stabilizers	Al, Ga, O, N, C, interstitial elements
β stabilizers	Mo, V, transition and noble metals
neutral	Sn, Zr

In the alloys α and β phases are separated by a two phase $\alpha+\beta$ region and with this region widens with increment in the solute amount. α alloys have HCP structure at room temperature and are known to have acceptable strength, toughness, creep resistance and weldability. Since they have HCP structure, they also do not have ductile-brittle transition temperature. β alloys are those that contain enough total alloying elements to keep the β phase in either a metastable or stable state after cooling to room temperature during heat treatment. In metastable β alloys, precipitation of second phase which mostly in form of α , takes place. Stable β alloys have more alloying elements and can not be hardened with aging. β alloys provides superior formability. However, they show ductile to brittle transformation and can not be used in low temperature applications. More than 100 titanium alloys have been developed so far. However, around 20 % of them have commercial standing. Among these alloys, almost half of the usage rate belongs to Ti-6Al-4V, which is closely followed by unalloyed titanium. Classification and composition of selected titanium alloys are given in Table 1.3 [1,13].

Table 1.3. Classification and composition of titanium alloys [1,13].

Class	Composition
Commercially pure (Cp), α alloys and near α alloys	Cp-Ti, 0.2Fe, 0.18O (Grade 1)
	Cp-Ti, 0.5Fe, 0.4O (Grade 4)
	Ti-5Al-2.5Sn
	Ti-6Al-2Sn-4Zr-2Mo-0.1Si
	Ti-6Al-2.7Sn-4Zr-0.4Mo- 0.4Si
	Ti-6Al-5Zr-0.5Mo-0.25Si 1020
$\alpha+\beta$	Ti-5.8Al-4Sn-3.5Zr-0.5Mo- 0.7Nb-0.35Si-0.06C
	Ti-6Al-4V
	Ti-6Al-6V-2Sn
	Ti-6Al-2Sn-2Zr-2Mo-2Cr- 0.25Si
	Ti-6Al-2Sn-4Zr-6Mo
	Ti-5Al-2Sn-2Zr-4Mo-4Cr
β alloys (metastable)	Ti-4.5Al-3V-2Mo-2Fe
	Ti-11.5Mo-6Zr-4.5Sn
	Ti-3Al-8V-6Cr-4Mo-4Z
	Ti-10V-2Fe-3Al
	Ti-15V-3Cr-3Al-3Sn

1.1.3 Metallographic preparation and electrolytic polishing of titanium alloys

Standard metallographic preparations can be applied to titanium alloys. Water cooled cutting with SiC or diamond cutting blades followed by grinding with SiC paper up to grit 2400, and finally polishing with colloidal silica would give satisfactory results for many titanium alloys. Kroll's reagent (1-3 ml HF, 5-6 ml HNO₃ and 100 ml H₂O) is the preferred etchant for titanium alloys. Although this recipe gives satisfactory results for many titanium alloys, pure titanium is extremely hard to polish mechanically and has a propensity to generate deformation surface layers, which could display false microstructures. Electropolishing process provides a solution to this problem [1].

By using electropolishing, it is practically possible to produce the smooth and bright surface finishes needed by the majority of titanium applications [14,15]. Electropolishing can produce surfaces that are microbiologically clean in addition to mirror-like, stress-free, and microscopically smooth surfaces because hydrogen is removed from the surface [16]. Electropolishing of titanium can also be used as a pre-treatment to further processes.

Titanium and its alloys have naturally occurring oxide layer with a surface thickness of a few nanometres on their surface. This dense oxide, which is typically in the form of amorphous TiO₂, has a fairly stable structure and chemical stability and serves as an anticorrosion layer. However, in terms of electropolishing, where a relatively high anodic dissolution rate is usually required, it can slow down anodic dissolution and thus efficiency [17].

In the electropolishing of titanium and its alloys, acidic electrolytes with hydrofluoric acid, perchloric acid, and sulfuric acid are most frequently utilized. Electrolytes based on perchloric acid known to be particularly successful at weakening the passive and dense oxide layer at the surface that can act as a barrier layer and slow the rate of anodic dissolution during electropolishing. On the other hand, electrolytes are hazardous due to their explosive or poisonous nature, and most of them also demand low process temperatures [18,19]. For this reason, alcohol-based electrolytes have been studied and used for electropolishing of titanium and alloys as safer substitutes for acid-based electrolytes [19–22]. Methanol is an excellent destabilizer of titanium oxide films. Ethanol similarly affects the oxide film and hence serves as a catalyst for the electropolishing process [23,24].

Electropolishing process is a type of electrolysis where work piece is used as anode that connected to positive terminal of power supply while a cathode material connected to the negative terminal. Electrochemical processes take place at the surface when a direct current is applied, reducing surface imperfections and leveling the morphology. Anodic dissolution and passivation are the two major mechanisms that control the electropolishing mechanism [25].

The passage of current causes the metal surface to selectively oxidize and dissolve during anodic dissolution. The surface is leveled and imperfections are eliminated as the dissolution happens preferentially at surface abnormalities such grain boundaries, dislocations, and impurities. The electrolyte composition, current density, temperature, and agitation are just a few of the variables that affect how quickly materials dissolve; these variables may all be adjusted to get desired surface finish. Parallel to anodic dissolution, passivation happens when a thin, continuous oxide layer forms on the valleys of the surface. This passivation layer serves as a protective barrier, preventing further breakdown and enhancing the valleys' ability to resist, thus also provides surface leveling [18,25,26].

1.1.4 Hot-dip aluminizing of titanium alloys

Titanium based materials have wide range of applications at elevated temperatures including highly oxidizing and corrosive service conditions. Even though natural oxide film of titanium is very stable at room temperature and resistant to corrosion and oxidation, it is very brittle at temperatures higher than 650 °C. Therefore, a protective layer at the surface would provide increased lifetime and performance for titanium based materials. For this purpose, various methods including Al films sputtering, magnetron sputtering, pack cementation, pack aluminizing have been researched so far. Amongst these methods, hot dip aluminizing is a promising method for coating titanium materials as it is a simple, quick and inexpensive alternative with respect to the other methods [27,28].

Hot dip aluminizing is a metallurgical process in which titanium alloy substrates are immersed in a bath of molten aluminum or aluminum alloy at elevated temperatures. Aluminum atoms penetrate into the titanium's surface throughout the process, creating intermetallic complexes, primarily titanium aluminides. By changing process variables including the bath temperature, immersion time, and aluminum alloy composition, it

is possible to regulate the aluminide layer's thickness and make changes to its composition. The microstructure of the intermetallic compounds created during hot dip aluminizing is distinctive and includes different phases including TiAl_3 and Ti_3Al , which help to improve the surface characteristics. In order to adapt the hot dip aluminizing process to particular applications, it is essential to comprehend the interaction between process parameters, microstructure, and surface alteration [29,30].

Titanium alloys' mechanical characteristics are dramatically impacted by hot dip aluminizing. The titanium alloy substrate's hardness, wear resistance, and high-temperature strength are all improved by the diffusion of aluminum into it. The development of intermetallic compounds also improves the material's ability to support loads and overall mechanical performance. Intermetallic compounds created during the process serve as a defense against hostile conditions such acids, high-temperature oxidation, oxidizing gases, and more.

1.2 Production and Properties of Titanium Dioxide

1.2.1 Anodic oxidation of titanium

Anodic oxidation is an electrochemical technique that uses an external electric field to control the oxidation of a metal. The cathode in anodization is a suitable material such as platinum or stainless steel, while the anode is a titanium substrate. An oxide layer develops on the titanium surface as a result of the application of a direct current (DC) voltage. Due to its great corrosion resistance and capacity to generate a persistent and adherent oxide layer, titanium exhibits exceptional anodization capabilities. TiO_2 , the natural oxide layer that covers the metal, acts as a barrier to prevent further oxidation. The oxide layer's thickness and quality are improved throughout the anodization process, which also enhances titanium's surface characteristics [31,32].

The anodic oxidation process and the properties of the resultant oxide layer are significantly influenced by the electrolyte selected. For the anodization of titanium, combinations of organic and inorganic acids are frequently utilized. Galvanostatic (constant current) and potentiostatic (constant voltage) anodization processes each provide unique benefits and levels of control over the oxidation process [33,34].

The anodic oxidation of titanium involves complex electrochemical reactions. Self-passivation causes a passive oxide layer to first develop on the titanium surface at low

voltages. The movement of metal cations and oxygen anions causes the oxide layer to thicken as the applied voltage rises. Voltage, current density, temperature, and electrolyte composition are a few examples of the variables that have an impact on the creation and growth of the oxide layer [32–34].

1.2.1.1 Anodic oxidation of titanium for producing TiO₂ nanotubes

Creation of highly organized TiO₂ nanotube arrays on the metal surface is made possible by anodic oxidation of titanium. Increased surface area, better coating adherence, and improved characteristics for numerous applications are just a few benefits of this special nanostructure. The formation of TiO₂ nanotubes through anodic oxidation of titanium expands the possibilities for surface modification and functionalization [2,35].

Formation of TiO₂ nanotubes during anodic oxidation follows a template-assisted growth mechanism. At first, a porous oxide layer with a network of linked nanopores forms on the titanium surface. These nanopores self-organize and develop vertically under particular anodization conditions, such as voltage, temperature, and electrolyte composition, leading to the creation of well-aligned nanotubes [8,36,37].

Development of TiO₂ nanotubes during anodic oxidation is influenced by a number of variables. These include the temperature, anodization period, composition of the electrolyte, and applied voltage. The length and diameter of the nanotubes are controlled by the voltage and anodization time, but the growth rate and shape are influenced by the electrolyte composition and temperature [6,35].

Characteristics of TiO₂ nanotubes can be changed by modifying the anodization parameters. It is possible to adjust the tube's diameter and length to suit a particular application's needs. Additionally, doping or introducing different substances during anodic oxidation can change the composition of nanotubes and improve particular qualities like optical or catalytic activity [9,38–40].

TiO₂ nanotubes offer a wide range of uses in several industries. They are useful for energy storage and conversion devices like dye-sensitized solar cells and lithium-ion batteries due to their large surface area and distinctive nanostructure. In addition, they perform effectively in the fields of medication delivery, sensing, and photocatalysis [10,41,42].

1.2.2 Photocatalytic properties of TiO₂

Due to its special qualities, including high stability, low toxicity, and widespread availability, TiO₂ has drawn a lot of interest as a versatile and effective photocatalyst. Initiating chemical reactions using light energy is a method known as photocatalysis. It has shown promise in solving a number of environmental problems, such as the purification of air and water, the creation of self-cleaning surfaces, and energy conversion [43,44].

TiO₂'s ability to produce electron-hole pairs when exposed to light with energy equal to or higher than its bandgap is principally responsible for its photocatalytic activity. A positively charged hole is left behind after an electron in TiO₂'s valence band is stimulated to the conduction band as a result of light absorption. The degradation of organic pollutants or the production of reactive oxygen species might subsequently occur as a result of these charge carriers taking part in a variety of chemical events, such as oxidation and reduction activities [45–47].

TiO₂'s photocatalytic activity is greatly influenced by a number of variables, including crystal structure, particle size, surface area, morphology, doping, and surface modifications. The photocatalytic characteristics of the anatase and rutile phases of TiO₂ also differ, with anatase being more active due to its higher surface reactivity. The effectiveness of light absorption and the accessibility of reactive sites are influenced by particle size and surface area. It is possible to improve TiO₂'s optical absorbance and charge carrier separation by doping it with foreign elements. The photocatalytic reaction can be extended to a wider spectrum range by adding organic sensitizers or deposition of noble metal nanoparticles [48–50]. Numerous methods have been used to improve the photocatalytic performance of TiO₂ photocatalysts in order to overcome their limits. These techniques involve the use of semiconductor heterostructures, such as TiO₂ in combination with other semiconductors, which facilitate effective charge separation and lessen electron-hole recombination. Additionally, surface alterations utilizing co-catalysts such noble metals or metal oxides might boost the photocatalytic effectiveness and charge transfer kinetics. Mesoporous structure design, the use of carbon components, and the application of photocatalysts that react to visible light are further strategies. Exploring and incorporating these enhancing techniques may result in the creation of TiO₂-based photocatalysts with increased functionality and efficiency [40,51–54].



2. MATERIALS AND METHOD

2.1 Electropolishing of CP-Ti Foils

Grade 4 Cp-Ti foils with the dimensions of 1 cm × 1 cm × 0.5 mm were ultrasonically cleaned in ethanol and distilled water for 10 min before electropolishing. The electrolyte solution was prepared by mixing 700 mL L⁻¹ ethyl alcohol, 300 mL L⁻¹ isopropyl alcohol, 50 g L⁻¹ aluminium chloride and 250 g L⁻¹ zinc chloride [21]. Electropolishing was carried out in an electrochemical cell in which the titanium sample was the anode while a stainless-steel plate served as the cathode. Distance between anode and cathode was kept constant at 3 cm. The electrolyte was agitated with a magnetic bar at a constant speed of 400 rev min⁻¹ during electropolishing except for one test in which the effect of agitation was investigated. The cell was powered by a unipolar DC power supply (Buehler Polimat 2), and electropolishing experiments were performed at various applied voltages in between 35 V and 75 V for a total electropolishing time of 1–8 min. Variation of current density during electropolishing processes was measured and recorded by a digital multimeter (Victor 86B). Electrolyte temperatures were kept constant at 12–35°C by the aid of flowing water during the entire processes. After electropolishing was completed, the samples were removed from the cell and ultrasonically cleaned in ethanol and distilled water for 10 minutes before characterisation. Surface morphology was examined by a Leica DM750 M optical microscope and a Hitachi TM1000 scanning electron microscope equipped with an energy dispersive spectrometer unit. Mean surface roughness was measured by a Veeco Dektak 6M surface profilometer. XPS (X-ray photoelectron spectroscopy) measurements were conducted with a Thermo K-Alpha X-Ray Photoelectron Spectrometer.

2.2 Hot-Dip Aluminizing of CP-Ti Foils

In this study aluminium coatings were prepared on Cp-Ti samples by hot dip aluminizing at two different (850-930 °C) temperatures. Two different pre-process

temperatures (25-400 °C) and two different cooling temperatures (25-400 °C) were used to reveal the effect of pre-heating and cooling rate on structural and morphological properties, and oxidation resistance of the coating. Process time was constant as 7.5 minutes. Table 2.1 shows the parameters for aluminizing process.

Table 2.1 : Hot dip aluminizing process parameters.

Sample ID	Pre-heating Temperature (°C)	Aluminizing Temperature (°C)	Cooling Temperature (°C)
a	25	850	400
b	400	850	25
c	400	850	400
d	25	930	400
e	400	930	25
f	400	930	400

Following hot dip aluminizing, properties of aluminium coating itself and that of titanium aluminium interface as well were investigated by optical microscope, scanning electron microscope (SEM), X-ray diffraction analysis (XRD) and high temperature oxidation tests. Samples are pre-treated at 650 °C for 1 hour prior to oxidation tests. Oxidation tests done in air atmosphere at 900 °C for up to 9 hours. Results were comparatively evaluated on the basis of process parameters.

2.3 Anodic Oxidation of CP-Ti Foils

2.3.1 Anodic oxidation with cyclic bipolar voltage

Cp-Ti foils in the dimensions of 2 cm x 1 cm x 0.4 mm were first cleaned by ethanol and distilled water in an ultrasonic agitator for ten minutes prior to electropolishing. Electropolishing was performed in an electrolyte containing ethyl alcohol (700 mL L⁻¹), isopropyl alcohol (300 mL L⁻¹), aluminum chloride (50 g L⁻¹) and zinc chloride (250 g L⁻¹) at 65V for 3 minutes. Anodic oxidation was performed with a two electrode configuration using the sample to be oxidized as the anode and a platinum wire as the cathode. Electrolyte used was the aqueous solution of 1% (vol.) HF. A bipolar DC power supply was used for the anodic oxidation. The positive voltage was always 20V, while the polarity was switched from positive level of 20V to zero. In one experiment, negative voltage was applied as -10V. The total processing time was 10 min. The amplitudes of positive voltage pulse and neutral period in one cycle (t^+ and t^0 ,

respectively) were varied, while the amplitude of negative voltage pulse (t^-) was applied as 200 μ s. The varying pulse amplitudes also vary duty cycle and frequency of the process. The ratio of the number of successive positive pulse to the number of neutral period or negative cycle (n_1/n_2) in one cycle was also varied. All processing parameters are given in Table 2.2 with the calculated values of duty cycle and frequency.

Table 2.2 : Cyclic bipolar voltage anodic oxidation process parameters.

V1 /V2, V	Amplitude of positive pulse, t^+ , μ s	Amplitude of neutral period, t^0 , μ s	Amplitude of negative pulse, t^- , μ s	Number of positive pulses/ number of neutral period or negative pulse n_1/n_2	Duty Cycle	Frequency, Hz
20/0	600	600	-	1/1	0.50	833
20/0	600	600	-	5/1	0.83	278
20/0	600	600	-	10/1	0.91	152
20/-10	600	400	200	1/1	0.50	833
20/0	1000	600	-	1/1	0.63	625
20/0	1000	1400	-	1/1	0.42	417

Following anodic oxidation, the samples were rinsed with distilled water, and annealed at 500 °C for 2 hours to obtain a crystalline structure. Morphologies of the samples were examined with Hitachi TM-1000 scanning electron microscope. X-ray diffraction patterns of the samples were determined with a GBC MMA 027 X-ray diffractometer. Water contact angle was determined by a KSV Instruments CAM 200 video camera-based contact angle meter.

2.3.2 Anodic oxidation with pre-deformed CP- Ti foils

Grade 4 Cp-Ti foils with the dimensions of 8 mm x 10 mm x 0.5 mm were cut. Afterwards the samples were cold deformed by two different processes. One group of samples was cold rolled with a strain of 10%, 30% and 50% as a thickness reduction, while uniaxial tension was applied to the other group with an axial strain of 2%, 5% and 8%. After the application of pre-deformation processes, the samples were ground with SiC papers (grit numbers 600, 800, 1000, 1200 and 2500), polished with colloidal silica (particle size of 0.05 μ m) and then cleaned first in ethanol and later distilled

water. Anodic oxidation was performed in an aqueous solution of 1 vol. % HF under a DC voltage of 20 V for 12 min. In the electrochemical cell, titanium sample was the anode while a 20 x 5 x 0.5 mm platinum plate served as the cathode. Distance between the anode and cathode was 3 cm. The electrolyte was agitated with a magnetic bar at a constant speed of 500 rpm during the anodic oxidation. Variation of the current density was measured and recorded by a digital multimeter (Victor 86B) during the process. Electrolyte temperature was constant around 25 °C during the process. At least two samples were anodized with the same parameters for each condition. After the anodic oxidation, the samples were washed with ethanol and distilled water. Prior to the characterization works, the samples were annealed at 450 °C to obtain crystalline anatase structure. Surface morphology was examined by FEI - Quanta FEG 250 scanning electron microscope (SEM) equipped with an Energy Dispersive Spectrometer (EDS) unit. X-ray diffraction (XRD) analysis was performed by scanning the samples over two theta angles of 30-75° with CuK α radiation on a GBC MMA 027 X-ray diffractometer operating under 35.5 kV and 28.5 mA. Williamson-Hall analysis was used for XRD patterns to estimate the crystallite size, and to quantify deformation induced microstrain on the samples. In order to compare the light absorption capabilities of the samples, UV-Vis diffuse reflectance spectra were recorded between 200-500 nm by a Shimadzu UV-2600 spectrophotometer. Photoluminescence analyses were performed for gathering information about exciton dynamics of the samples on a Perkin-Elmer LS-55 spectrophotometer by collecting emission in the range of 280-500 nm from the sample excited by 240 nm wavelength light. In order to observe the ability of the samples to decompose a model pollutant, MB degradation tests were conducted. For these tests, 1 cm² samples were first placed in a beaker containing 10 mg/L aqueous solution of MB, and irradiated by an 8 W power lamp emitting 365 nm wavelength ultraviolet light up to 4 h. MB degradation was evaluated by the absorbance measurements at 665 nm performed on a Perkin Elmer Lambda-9 UV/VIS/NIR spectrophotometer. All characterization tests were duplicated.

2.3.3 Anodic oxidation with carbon structure added electrolytes

Samples with the dimensions of 10 mm x 10 mm x 0.5 mm were cut from a Grade 4 Cp-Ti plate. For the surface preparation, they are grounded with SiC papers (grit numbers 600, 800, 1000, 1200 and 2500), polished with colloidal silica (particle size

of 0.05 μm) and then cleaned first in ethanol and later in distilled water. Anodic oxidation was performed in an aqueous solution of 0.5 M HF with addition of three different amounts (0.025, 0.030 and 0.035 g/L) of CNT, and a reference sample was prepared with anodic oxidation within a 0.5 M HF electrolyte without any addition of CNTs. The CNTs used in this study were MWCNTs with average outer diameter of 9.5 nm and length of $\sim 1.5 \mu\text{m}$. They are from Grafen Chemical Industries and was produced via catalytic carbon vapor deposition method. Anodic oxidation time and voltage was 12 minute and 20 V respectively. Electrochemical cell with two electrodes was used with CP-Ti sample as anode and a 20 mm x 5 mm x 0.5 mm platinum plate as the cathode with 3 cm between them. The electrolyte was agitated with a magnetic bar at a constant speed of 500 rpm and electrolyte temperature was constant around 25°C during the anodic oxidation. A digital multimeter (Victor 86B) was utilized to record variation of the current density during anodic oxidation. After the anodic oxidation, the samples annealed at 450 °C to obtain crystalline anatase structure. Surface morphology of produced composites was examined by FEI - Quanta FEG 250 scanning electron microscope (SEM) equipped with an Energy Dispersive Spectrometer (EDS) unit. A Horiba Jobin Yvon HR8000 UV micro-Raman spectrometer with a 632 nm laser was used to determine the raman spectrum of samples for verifying MWCNT presence on the TiO_2 nanotube surface. Diffuse reflectance spectroscopy was utilized with a Shimadzu UV-2600 spectrophotometer by recording UV-VIS absorbance spectra between 200 and 500 nm in order to compare the samples' capacities for light absorption. With a Perkin-Elmer LS-55 spectrophotometer, photoluminescence investigations were carried out to learn more about the samples' exciton dynamics. Emission in the range of 280–500 nm from the samples stimulated by 240 nm light was collected for photoluminescence tests. MB degradation experiments were carried out to see how well the samples could mineralize a model pollutant. In order to conduct these tests, samples having 1 cm^2 surface area were first put into a beaker containing a 10 mg/L aqueous solution of MB. The samples were then exposed for 4 hours to 365 nm UV radiation from an 8 W power lamp. Perkin Elmer Lambda-9 UV/VIS/NIR spectrophotometer were used to assess MB degradation rates by doing absorbance measurements at 665 nm with the treated MB solutions.



3. RESULTS AND DISCUSSIONS

3.1 Electropolishing of CP-Ti Foils

In the typical polarisation behaviour of titanium, the process can be divided into three main stages, each of which can be described by the following reactions:



During the electropolishing of titanium, Eqs. 3.1 and 3.2 often take place simultaneously [22]. At a low applied voltage, oxide thickness is low, and oxide is possibly dissolved at a higher rate than of its formation rate [18] and thus direct material removal takes place from bare metal to the electrolyte. As the applied voltage increases, the formation rate of passive oxide film formed through Eq. 3.2 and its dissolution rate are balanced resulting in a constant current region. At higher applied voltage levels, the transpassive region is achieved where oxygen evolution takes place through Eq. 3.3. As a result, electropolishing is progressed through the oxide layer and achieving a good electropolishing would be due to a balance between continuous formation and dissolution of the oxide layer [18].

Figure 3.1a shows variation of current density with increasing processing time up to 3 min for various applied voltages. In order to see possible effect of the agitation, variation of the current density during electropolishing at 65 V in the non-agitated electrolyte was also included. At the lowest applied voltage (35 V) in the present study, current density was almost constant from the beginning up to the end of the process. This indicates that a good balance between the formation and dissolution of the oxide was maintained during the entire electropolishing. For the electropolishing performed at 65 V in the agitated electrolyte, current density continuously increases up to the end of the process, exhibiting some minor fluctuations. In contrast, when the electrolyte is not agitated at this voltage level, current density starts to decrease from the 120th and

goes down with a decreasing trend up to the end of the process. Even though the electrolyte is agitated, a similar trend of the current density was observed at 75 V with an earlier onset of the current density decrement (at about the 95th). High applied voltages such as 65 V and 75 V increase oxide film formation and promote oxygen evolution during the electropolishing process [55,56]. Current observations presented in Figure 3.1a suggest that at 65 V (with agitation), the dissolution rate of oxide layer is higher than its formation rate, resulting in a continuous increment in the current density. At this point, it is also worth noting the clear effect of agitation at 65 V. Without agitation, it seems to be difficult to remove the oxide layer from the surface which slows down anodic oxide film dissolution, [17,21,57] increases electrical resistance and finally results in the current density decrement. In a similar manner, at 75 V where the oxide film thickness would be higher, even if the electrolyte was agitated, this agitation might be insufficient to remove oxide layer and thus current density decreases.

From the view point of electrolyte temperature, the current density increases as the initial electrolyte temperature increases without any significant change in the general trend of the curve (Figure 3.1b). It is noted that current density increases exponentially with the increment of electrolyte temperature [58]. Although any exponential increase was not observed in the present work, decrement of electrical resistance with increasing electrolyte temperature clearly indicates that oxide layer dissolution might take place at a higher rate than that of its formation at a higher electrolyte temperature.

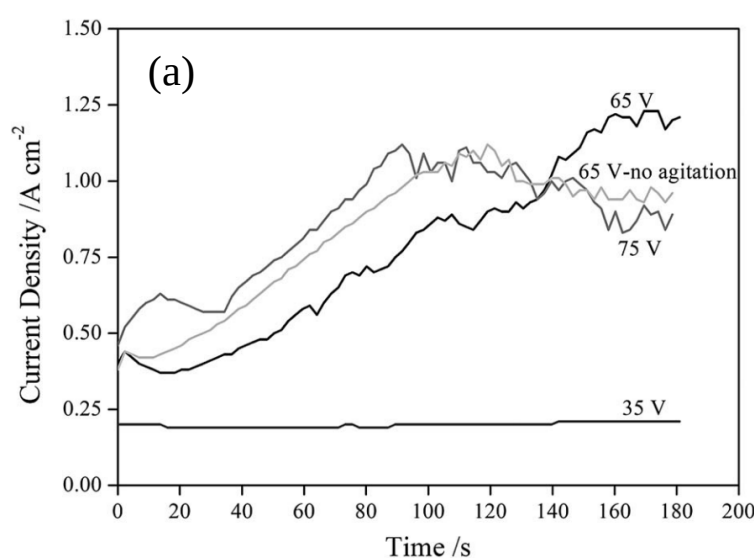


Figure 3.1 : Variation of current density with processing time for (a) various applied voltages and (b) different initial electrolyte temperature.

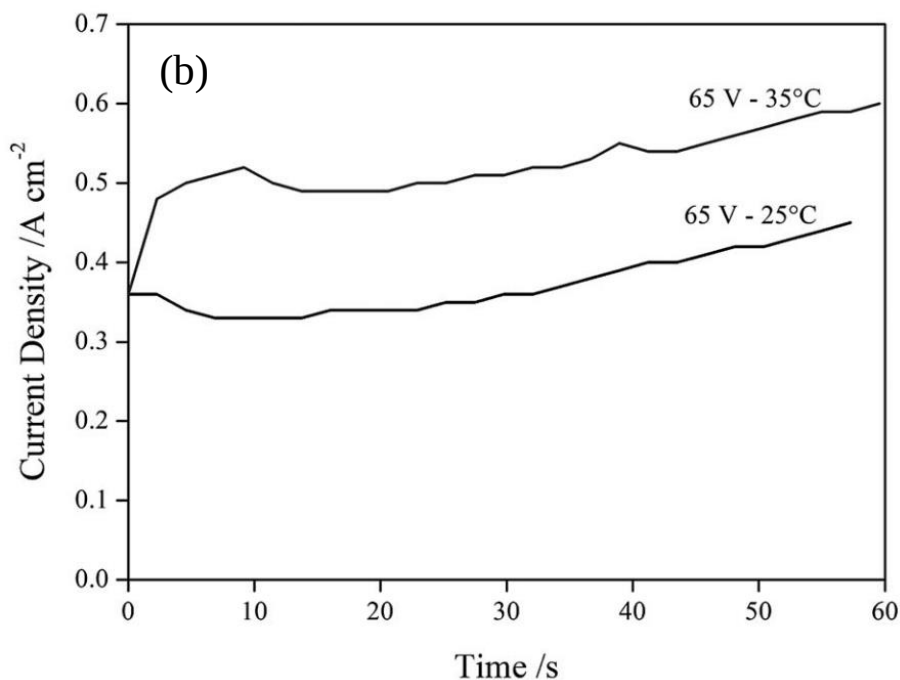


Figure 3.1 (continued) : Variation of current density with processing time for (a) various applied voltages and (b) different initial electrolyte temperature.

Figure 3.2 shows optical micrographs of the samples, which were electropolished with different processing parameters, along with that of the untreated sample (Figure 3.2a) for comparison. It is first noted that the samples electropolished for shorter times at a given voltage do not have a smooth appearance due to surface irregularities (Figure 3.2b, 3.2c, 3.2e, 3.2f, 3.2j). Surface irregularities are natural consequences of peaks and valleys on the substrate surface. Because the thickness of the oxide layer is higher at the valleys than at the peaks, the electrical resistance would be also higher at valleys, and thus the valleys would dissolve later than the peaks, resulting in the levelling of the surface [18]. As the processing time increases, these irregularities disappear and a more uniform and even surface appearance is achieved (Figure 3.2d, 3.2g, 3.2k). The processing time that is required for the almost complete removal of these irregularities is a function of the applied voltage. It takes about 8 min at 35 V, 3 min at 65 V, and 2 min at 75 V. When the processing time at 75 V was further increased to 3 min (Figure 3.2l), the surface starts to deteriorate again and becomes covered with an oxide layer, later confirmed with EDS results. On the other hand, from the comparison of the micrographs of the electropolished samples with and without agitation (Figure 3.2g, 3.2h), it is seen that the surface is not uniform when electropolishing is performed without agitation and is covered with an oxide layer again. From the view point of

electrolyte temperature, it is clear that increasing electrolyte temperature is beneficial to reduce surface irregularities (Figure 3.2e, 3.2i). Increasing of initial electrolyte temperature increases current density and decreases oxide layer on the surface as well. Because higher current density results in faster and denser oxide formation and dissolution, by increasing electrolyte temperature, the electropolishing process can be accelerated to obtain a desired surface finish.

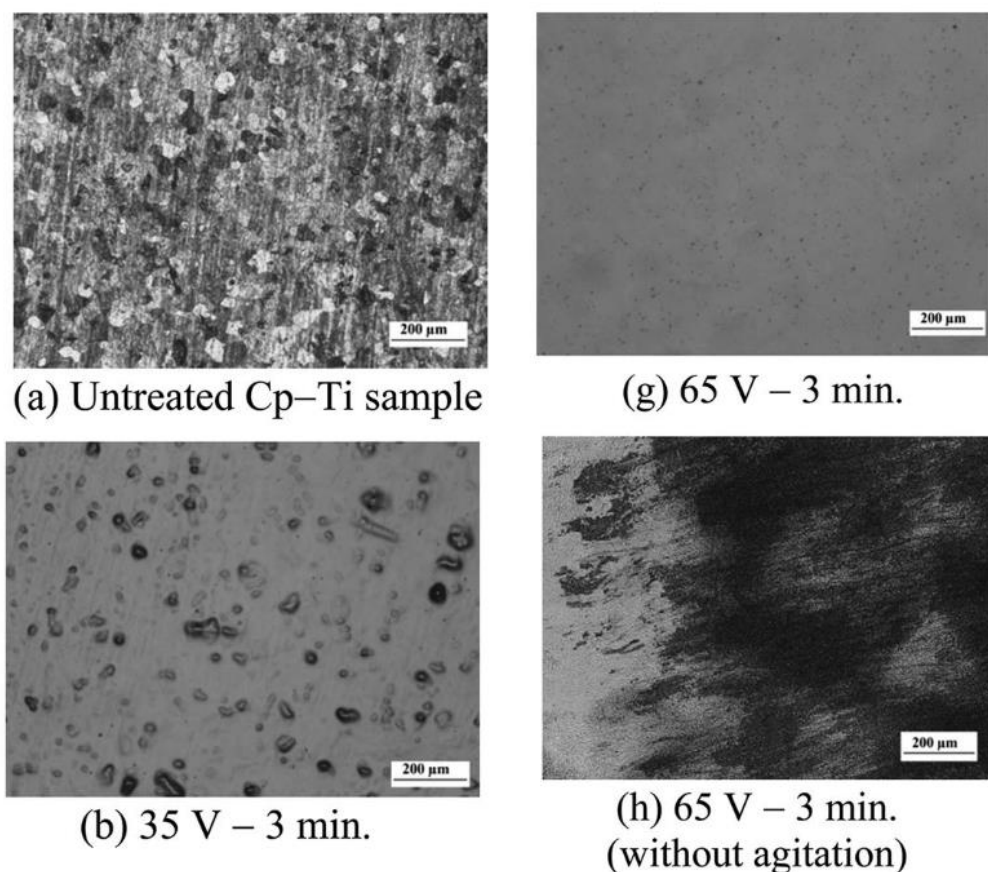
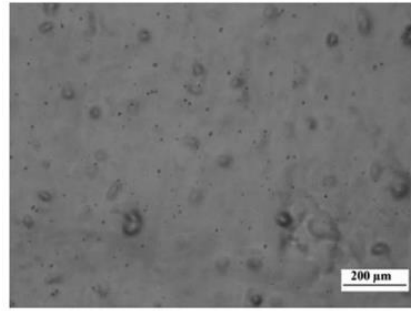
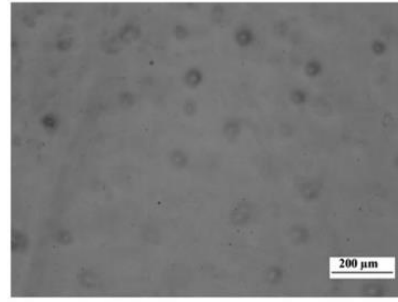


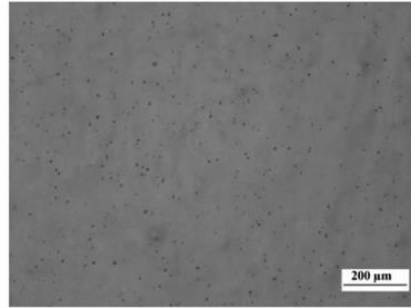
Figure 3.2 : Optical micrographs of untreated and electropolished samples
 (a) untreated Cp-Ti sample; (b) 35 V – 3 min; (c) 35 V – 5 min; (d) 35 V – 8 min; (e) 65 V – 1 min; (f) 65 V – 2 min; (g) 65 V – 3 min; (h) 65 V – 3 min (without agitation); (i) 65 V – 1 min (35°C); (j) 75 V – 1 min; (k) 75 V – 2 min; (l) 75 V – 3 min.



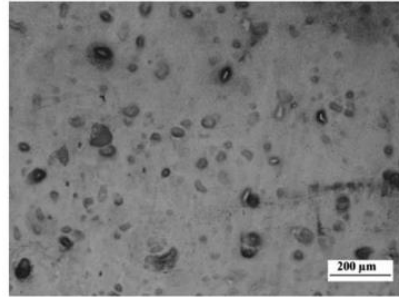
(c) 35 V – 5 min.



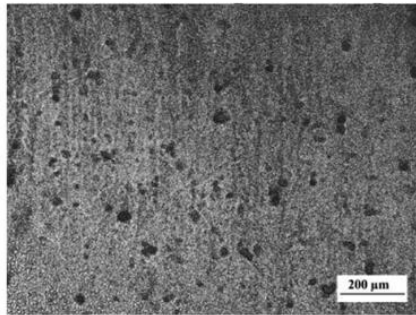
(i) 65 V – 1 min
(35°C)



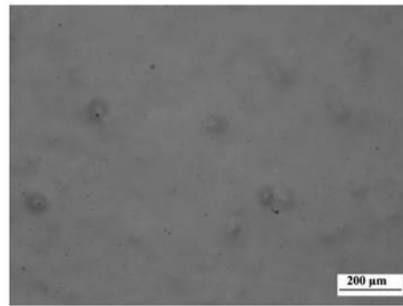
(d) 35 V – 8 min.



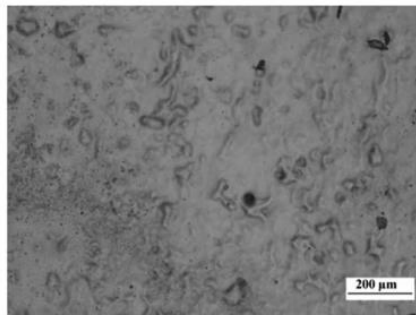
(j) 75 V – 1 min.



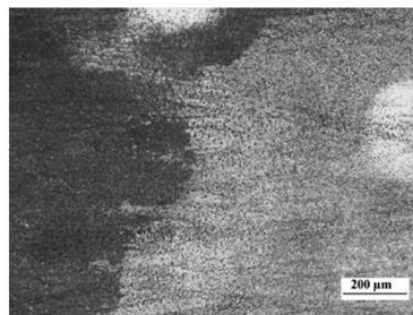
(e) 65 V – 1 min.



(k) 75 V – 2 min.



(f) 65 V – 2 min.



(l) 75 V – 3 min

Figure 3.2 (continued) : Optical micrographs of untreated and electropolished samples (a) untreated Cp-Ti sample; (b) 35 V – 3 min; (c) 35 V – 5 min; (d) 35 V – 8 min; (e) 65 V – 1 min; (f) 65 V – 2 min; (g) 65 V – 3 min; (h) 65 V – 3 min (without agitation); (i) 65 V – 1 min (35°C); (j) 75 V – 1 min; (k) 75 V – 2 min; (l) 75 V – 3 min.

Figure 3.3 shows the mean surface roughness measured by a stylus-type surface profilometer. It can be clearly seen that certain voltage and time combinations provide a satisfactory electropolishing quality (in terms of lower mean surface roughness). These combinations are 35 V–8 min, 65 V –3 min and 75 V–2 min, and correspond to a 40–60% decrement in the mean surface roughness with respect to that of the untreated surface. It should be noted that all these combinations are valid for the agitated electrolytes. The polishing process actually commences by smoothening and brightening actions which occur simultaneously by the removal of larger and smaller peaks, respectively [26]. Based on this statement, it can be said that some samples with non-uniform surface finishes including 65 V–3 min without agitation, can exhibit some improvement in terms of smoothening (a decrement in mean surface roughness) by removal of larger surface irregularities. However, they do not have enough improvement in terms of brightening, which requires further eliminating of smaller surface peaks.

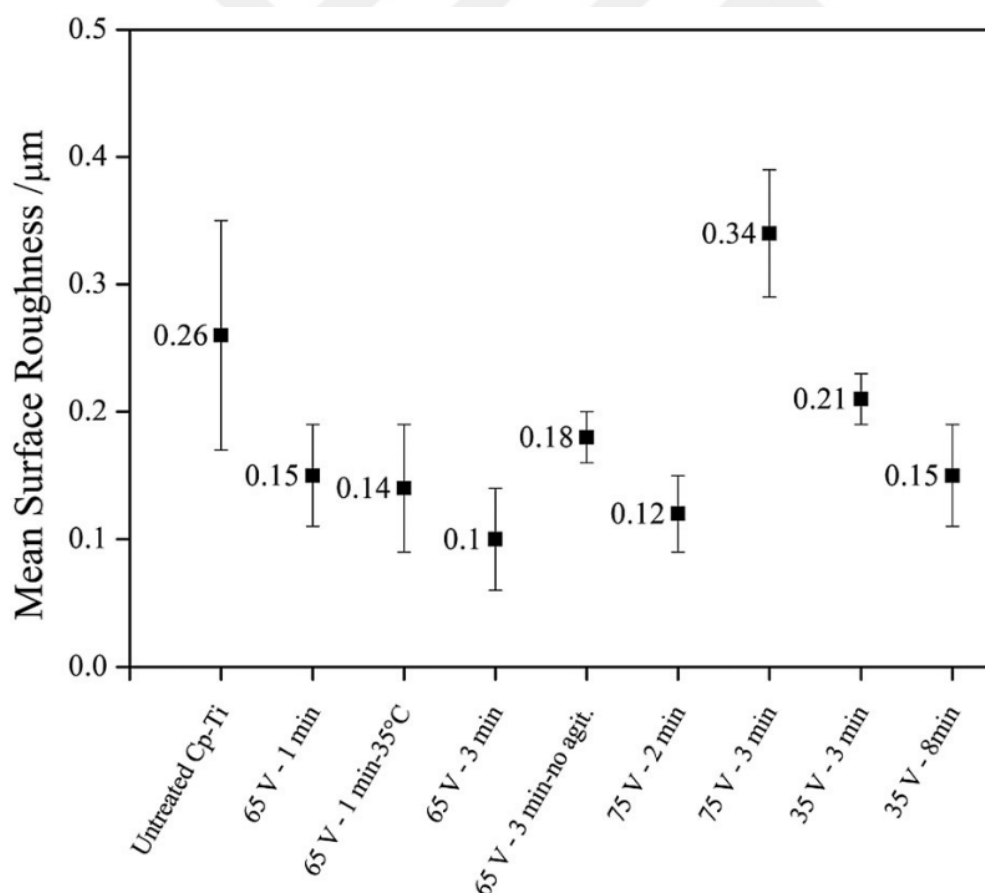
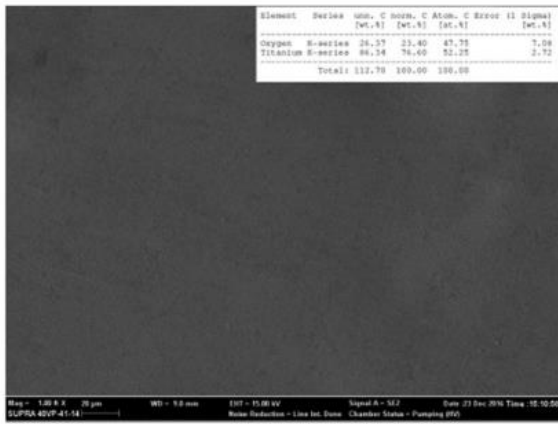
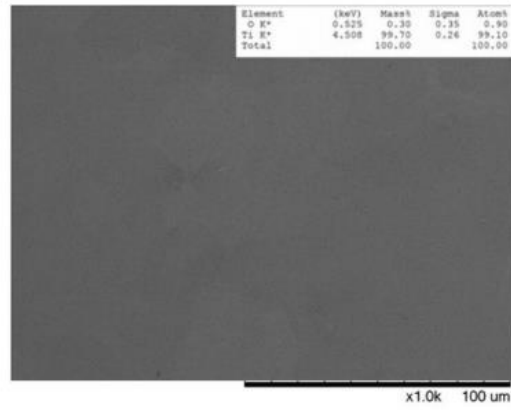


Figure 3.3 : Mean surface roughness of the untreated and electropolished samples.

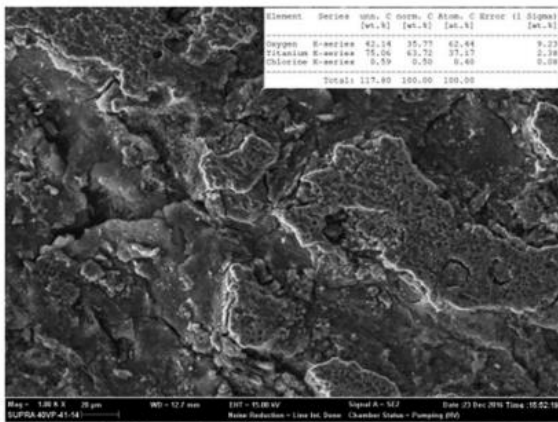
Figure 3.4 shows SEM micrographs and EDS analysis of the electropolished surfaces. General area EDS results of the samples electropolished at 65 V for 3 min without agitation (Figure 3.4a) and at 75 V for 3 min (Figure 3.4b) show the presence of oxygen at the surface confirming the existence of an oxide layer. 65 V–3 min (Figure 3.4c) and 35 V–8 min samples (Figure 3.4d) in the agitated electrolyte contain very low to no oxygen which indicates uniform surfaces have very low to no oxygen content. EDS results of 65 V–1 min sample electropolished at 35 °C (Figure 3.4e) and 65 V–1 min sample electropolished at 25 °C (Figure 3.4f) show the effect of initial electrolyte temperature. While the 65 V–1 min sample electropolished at 25 °C contains a high amount of oxygen, the 65 V–1 min sample electropolished at 35 °C contains very low to no oxygen. Also, small area EDS results show that valleys of the surface (Figure 3.4g) contain higher amounts of oxygen than the peaks (Figure 3.4h) where the electrical resistance is expected to be lower. Oxide layer present on 1 min sample (Figure 3.4f) at 65 V was mostly removed with increasing processing time to 3 min (Figure 3.4c). This indicates that longer durations at a certain voltage level may help in reducing oxygen content on the surface. However, it is known that higher applied voltages induce very rapid and dense oxide formation [55] and such oxides may not be removed even with agitation after a certain time of processing. As a result, if the process goes on after a specific time at a certain voltage, the surface would be covered with the oxide layer again, as clearly seen from the 75V–3 min sample (Figure 3.4b). When this oxide layer cannot be removed from the surface, it clearly hinders the electropolishing process. Nonetheless, even at the highest voltage used in this study (75 V), which has a potential to produce a dense oxide layer, satisfactory electropolishing was achieved up to an electropolishing time of 2 min by agitating the electrolyte. However, without agitation, satisfactory electropolishing would not be achieved at all.



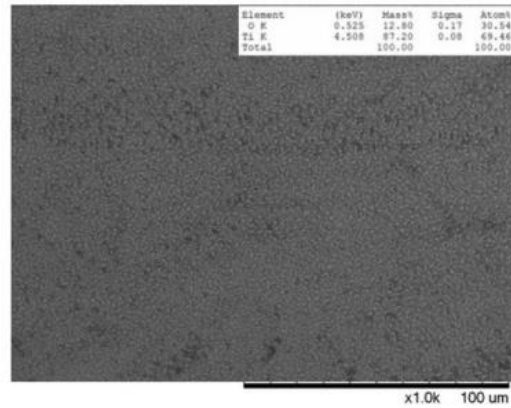
(a) 65V – 3 min. (without agitation)



(e) 65V-1 min (electropolished at 35°C)

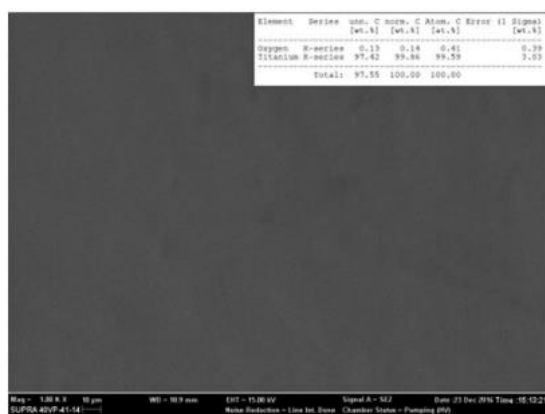


(b) 75V – 3 min

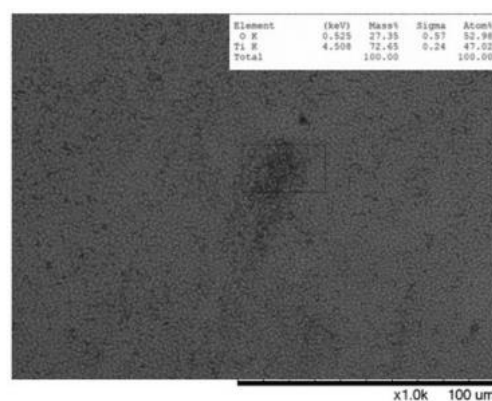


(f) 65V-1 min (electropolished at 25°C)

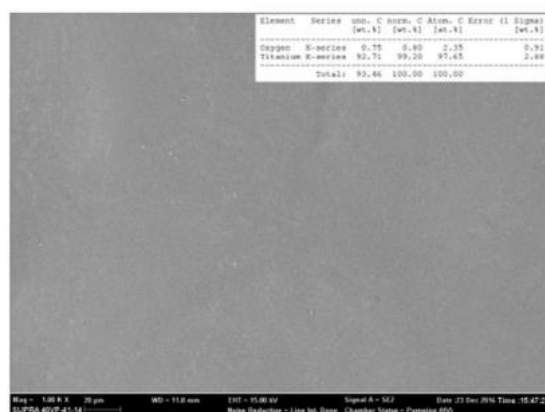
Figure 3.4 : SEM micrographs and EDS analysis of the electropolished samples: (a) 65 V–3 min (without agitation); (b) 75 V–3 min; (c) 65 V–3 min (with agitation); (d) 35 V–8 min; (e) 65 V–1 min (electropolished at 35°C); (f) 65 V–1 min (electropolished at 25°C); (g) 65 V–3 min valleys (without agitation); (h) 65 V–3 min peaks (without agitation).



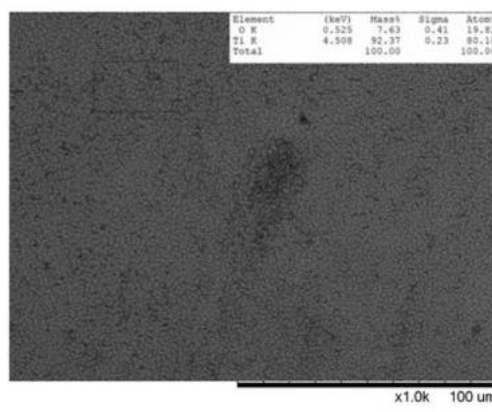
(c) 65V – 3 min. (with agitation)



(g) 65V-3 min-valleys (without agitation)



(d) 35V – 8 min.



(h) 65V-3 min-peaks (without agitation)

Figure 3.4 (continued): SEM micrographs and EDS analysis of the electropolished samples: (a) 65 V–3 min (without agitation); (b) 75 V–3 min; (c) 65 V–3 min (with agitation); (d) 35 V–8 min; (e) 65 V–1 min (electropolished at 35°C); (f) 65 V–1 min (electropolished at 25°C); (g) 65 V–3 min valleys (without agitation); (h) 65 V–3 min peaks (without agitation).

Figure 3.5 shows XPS Ti2p and survey spectra of selected electropolished sample surfaces. XPS analysis was conducted to compare the outermost surfaces of the samples. Survey spectra results show that the 65V–3 min (Figure 3.5a), 65V–3 min (Figure 3.5b) and 75V–3 min (Figure 3.5c) samples outermost surface structure similarly contains Ti, O and C elements. Contamination from the environment can be the reason for the presence of C element. Detailed analysis of the Ti XPS spectra (Figure 3.5d, 3.5e, 3.5f) suggests that outermost surfaces are covered with titanium oxide films. Owing to the nature of XPS analysis, this thin oxide layer (analysis depth 1–5 nm) can be attributed to naturally occurring oxide of titanium or it could be formed during the electropolishing process. Two peaks at 464.08 and 458.19 eV binding energies indicate Ti^{4+} –O bonding which suggests the presence of TiO_2 , while the peak

at the 453.44 eV binding energy is indicating the presence of unoxidised Ti. Even though micrographs and EDS results of the selected samples are quite different from each other, XPS analysis results are very similar and clearly on all samples selected there is an oxide layer covering the electropolished surface with traces of unoxidised Ti. Combining XPS and EDS results gives a better understanding of the near surface region of the samples. From XPS results, there is not much difference at the surfaces of the samples. However, EDS results clearly indicate that smooth and uniform surfaces contain lower oxygen content than non-uniform surfaces.

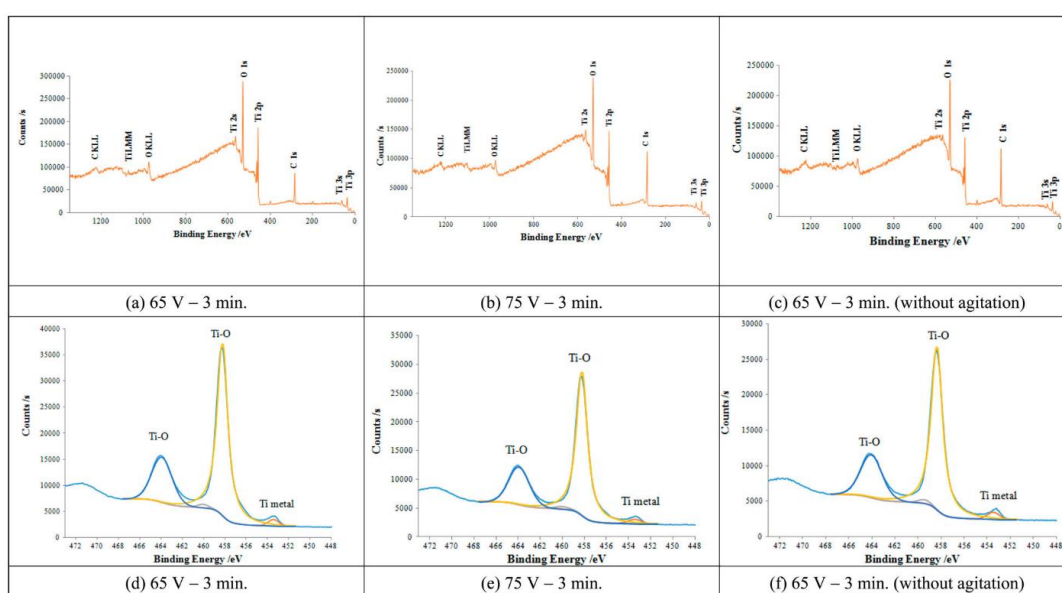


Figure 3.5 : XPS Ti₂p and survey spectra of selected samples: (a) 65 V–3 min; (b) 75 V–3 min; (c) 65 V–3 min (without agitation); (d) 65 V–3 min; (e) 75 V–3 min; (f) 65 V–3 min (without agitation).

3.2 Hot-Dip Aluminizing of CP-Ti Foils

Figure 3.6 shows the optical micrographs of the samples with different process parameters. Figure 3.6a, 3.6b, 3.6c shows samples that hot dip aluminized at 850 °C while Figure 3.6d, 3.6e, 3.6f shows samples that hot dip aluminized at 930 °C. For Figure 3.6a and 3.6d, the samples was not preheated before the aluminizing, while they were slowly cooled in the furnace from 400 °C after the aluminizing. Figure 3.6b and 3.6e samples was preheated to 400 °C before the aluminizing, while they were fast cooled in air after the aluminizing. Also Figure 3.6c and 3.6f samples was preheated to 400 °C before the aluminizing while they were also slowly cooled from 400 °C after the aluminizing. Figure 3.7 shows the SEM micrographs of the same samples in the same order.

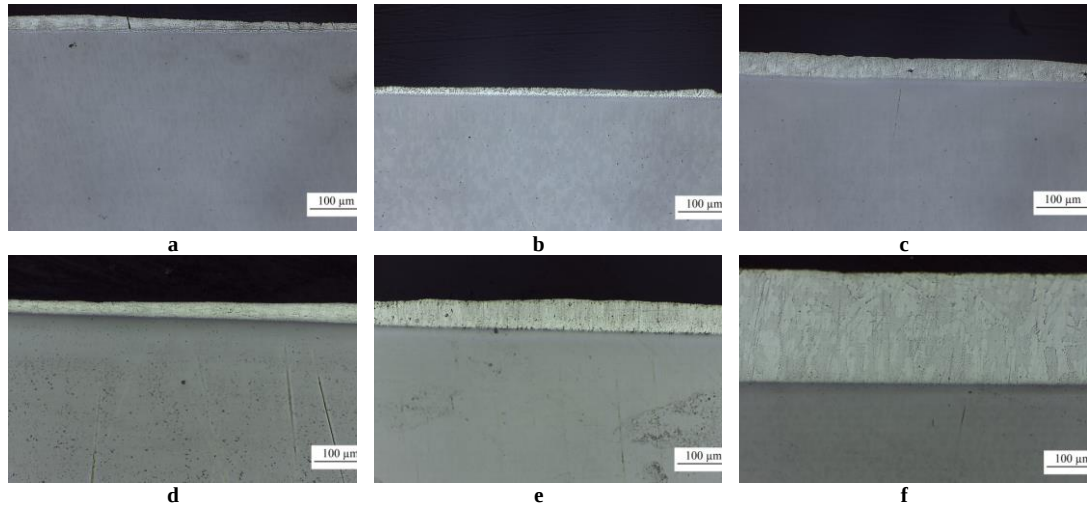


Figure 3.6 : Optical micrographs of the hot dip aluminized samples.

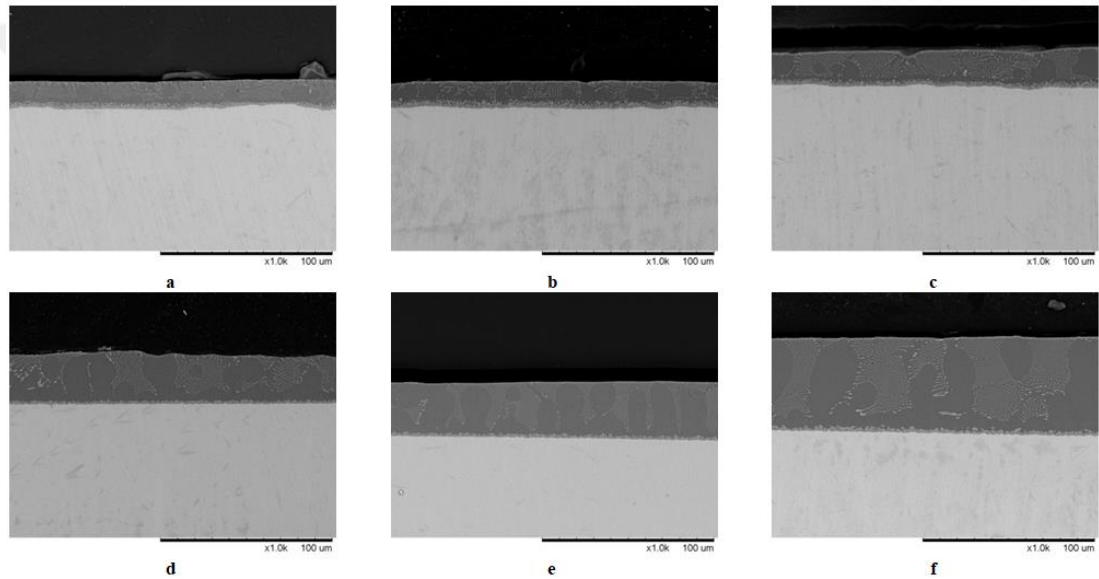


Figure 3.7 : SEM micrographs of the hot dip aluminized samples.

Figure 3.8 shows the variation of coating thickness with process parameters. In this graphic O marking refers to room temperature and F marking refers to 400 °C. So OF marking means that the samples were at room temperature before the aluminizing, and slowly cooled from 400 °C after the aluminizing. FO marking means that the samples were at 400 °C before the aluminizing, and fast cooled in air after the aluminizing. And, FF marking means that the samples were preheated to 400 °C before the aluminizing, and slowly cooled from 400°C after the aluminizing. It is clear that coating thickness increases with the increase in the aluminizing temperature. Also preheating and slow cooling have a thickness increasing effect.

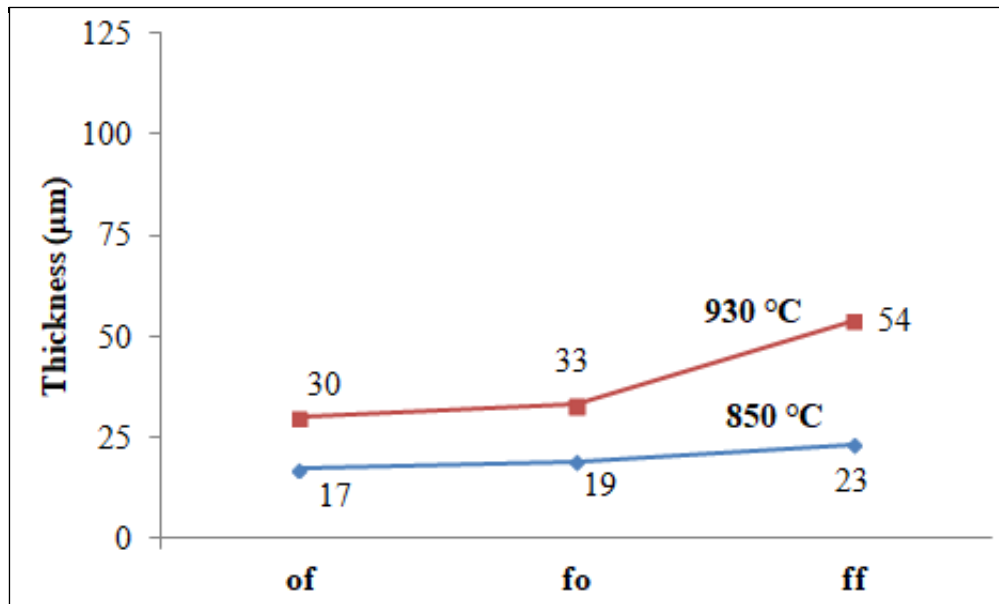


Figure 3.8 : Variation of coating thickness with the aluminizing parameters.

Figure 3.9 shows XRD patterns of the hot dip aluminized CP-Ti samples. At all samples near surface area of the samples contains titanium – aluminium intermetallic phases as well as and aluminium and titanium metallic phases. However intensity of these phases differentiate with the aluminizing process parameters, which indicate structure of the coatings produced on the titanium samples are different from each other.

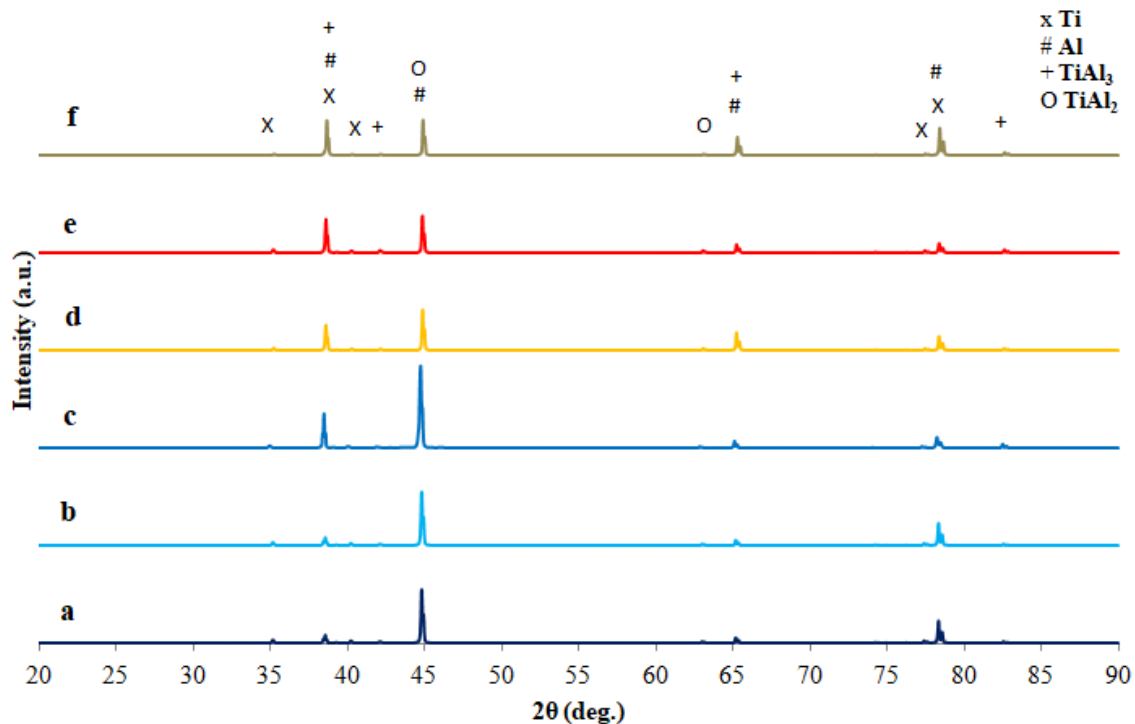


Figure 3.9 : XRD patterns of hot dip alumized samples.

Figure 3.10 shows the percent weight change of the hot dip aluminized Cp-Ti samples with time during the oxidation tests at 900 °C. It is clear that oxidation resistance of titanium is highly improved with all process parameters. Lower aluminizing process temperatures produce higher oxidation resistant coatings compared to higher temperature processes. Preheating the samples before the aluminizing process increases final coating oxidation resistance.

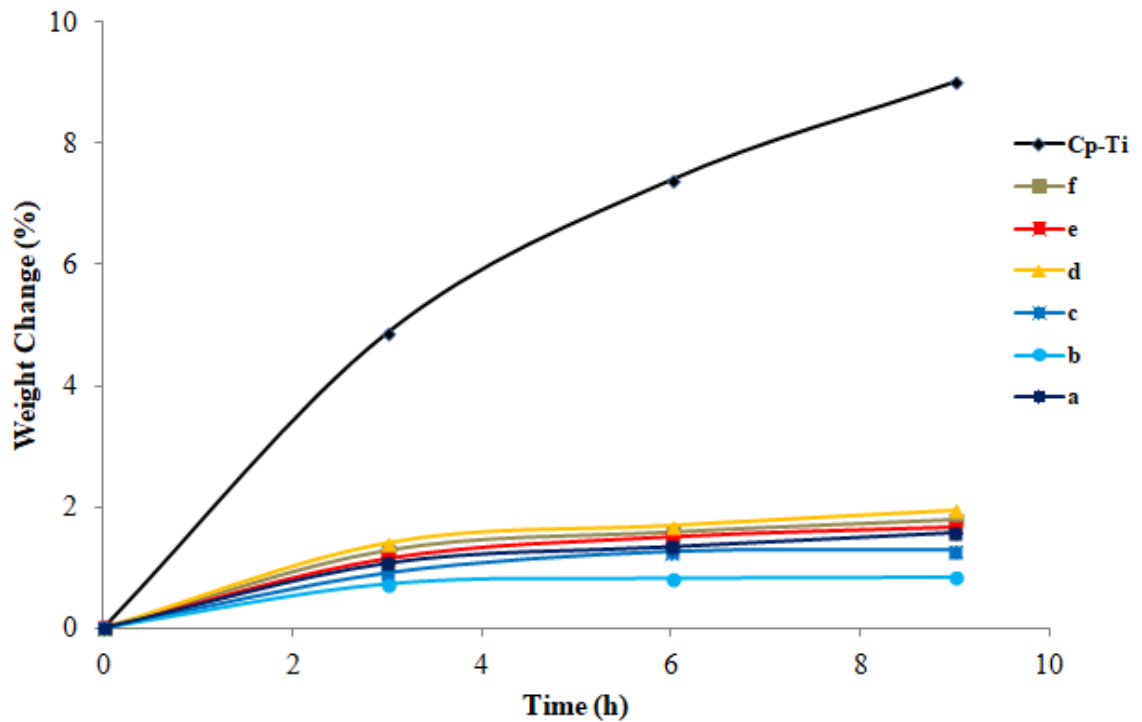


Figure 3.10 : Weight change of the hot dip aluminized samples with the oxidation time.

3.3 Anodic Oxidation of CP-Ti Foils

3.3.1 Anodic oxidation with cyclic bipolar voltage

Figure 3.11 shows variation of current density with the anodic oxidation time for different process parameters. In all process parameters, similar behavior of current density variation was observed. Current density increased rapidly at the beginning of the process and then reached to a steady state value. This behavior is common for anodization process performed in fluoride containing electrolytes. Generally three stages are observed during anodization in fluoride containing electrolytes. In the first stage, current drops quickly due to formation of barrier oxide layer. In the second step surface becomes locally activated and porous structure starts to form which is

identified with sudden current increase. At the third and last step, a steady state current is achieved due to self-ordering of the pores with equally sharing available current [10,59,60]. Level of this steady state value strongly depends on the electrical parameters applied during the process. It can be clearly seen that increasing amplitude of the positive pulse (Figure 3.11b and 3.11c), and increasing numbers of successive positive pulses (Figure 3.11b, 3.11d and 3.11e) in one cycle decreased steady state current density. It is also apparent from Figure 3.11b, 3.11d and 3.11e that increasing duty cycle (decreasing frequency) decreased steady state current density. On the other hand, it can also be seen that increasing amplitude of the neutral period decreased current density (Fig. 3.11c and 3.11f). Finally, by comparing Fig. 3.11b and 3.11a, it is clear that application of negative voltage significantly increased current density. From these observations and frequency values given in Table 2.2, it can be stated that increasing frequency generally leads to current density increment.

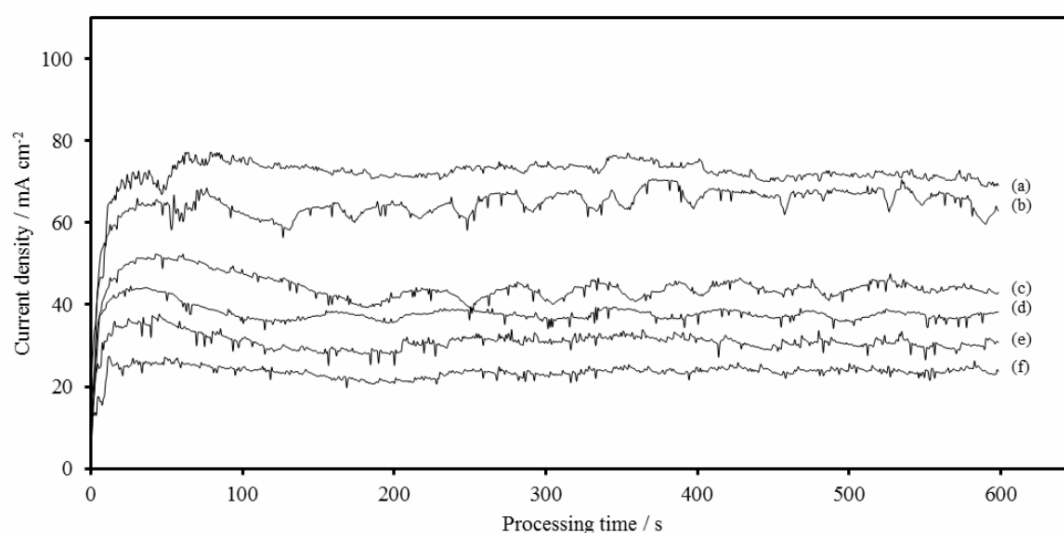


Figure 3.11 : Variation of current density as a function of anodic oxidation time.

Figure 3.12 shows surface SEM micrographs of the anodic oxidation samples. It is clear that nanotube morphology was obtained for all process parameters (except Figure 3.12d where a negative voltage of -10V was applied). Pore diameters varied in between 20-100 nm. It has been known that increasing anodic oxidation voltage results in an increased pore diameter [61]. From the comparison of Figure. 3.12a, 3.12b and 3.12c, it can be seen that when number of successive positive pulses was increased, pore diameter slightly increased and pore irregularities (varying pore size and morphology) became more pronounced as well. Similarly, it is clear from Figure 3.12e and 3.12f

that increasing amplitude of neutral period also increased nanotubes diameter and their irregularity. The smallest pore size (~ 20 nm) was obtained from the sample shown in Figure 3.12e, which was anodized by using the highest positive pulse amplitude ($1000 \mu\text{s}$), while the highest pore size (~ 100 nm) was obtained from the sample shown in Figure 3.12f, which was anodized by using the highest amplitude of the neutral period ($1400 \mu\text{s}$). When the negative voltage of -10V was applied, nanotubes morphology was deteriorated, and random sponge like structure was obtained (Figure 3.12d). It has been known that at higher anodizing voltages in HF based electrolytes nanotube structure is replaced by sponge like random nano porous structure [41]. It was demonstrated in this work that application of a negative voltage also resulted in a sponge like structure.

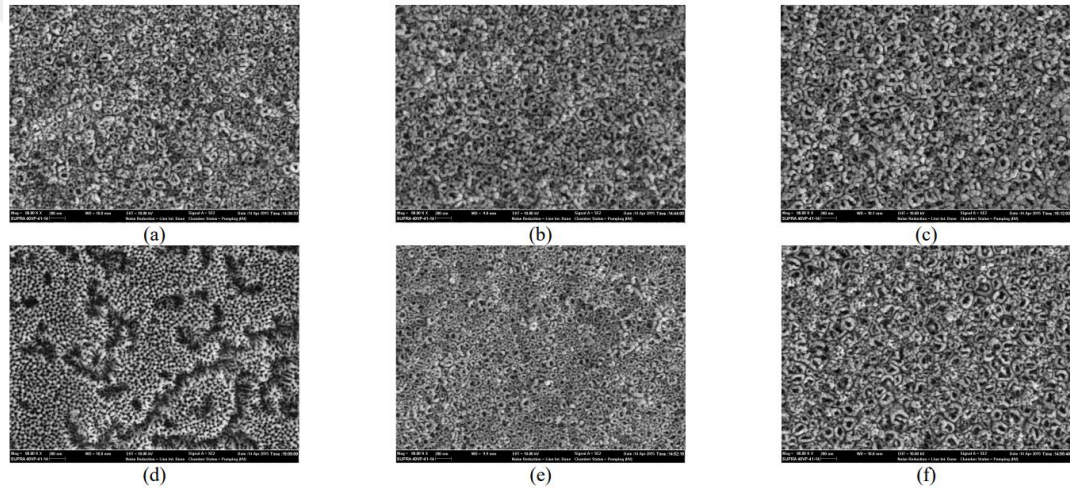


Figure 3.12 : SEM micrographs of anodic oxidized samples

Figure 3.13 shows the XRD patterns of the anodized samples after annealing. Regardless of the anodic oxidation parameters, all samples showed TiO_2 anatase peaks in addition to strong titanium peaks coming from the titanium substrate. It should be noted that there were no clear difference amongst the samples in terms of relative intensity of anatase and titanium peaks. It suggests that processing parameters used in the present work, although they affect the surface morphology, they have no clear effect on the type and intensity of the phases formed at the surface.

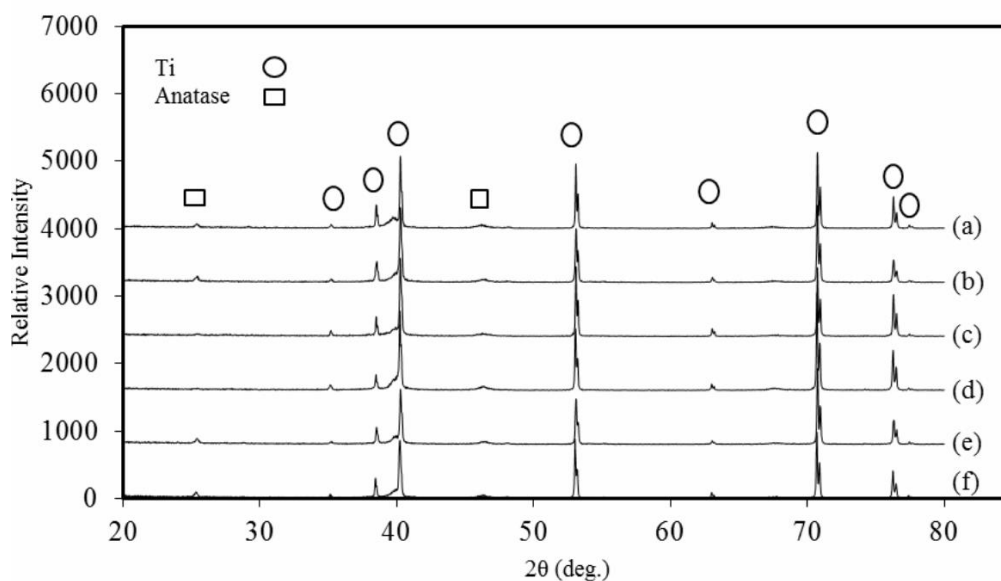


Figure 3.13 : XRD patterns of anodic oxidized samples after annealing.

Figure 3.14 shows water contact angles of the samples anodized by using the parameters given in Table 2.1 with that of as-electropolished sample for comparison. It was shown that as-electropolished samples have the highest contact angle (85°), while the anodized samples have lower contact angle values. It clearly suggests that anodic oxidation performed in aqueous solution of 1% (vol.) HF strongly reduced the contact angle by increasing hydrophilicity of the anodized surface. Water contact angle of the anodized surfaces was reduced 55% and 85% with respect to as-electropolished state. However, it could not be observed a systematic correlation between the contact angle values and anodic oxidation parameters.

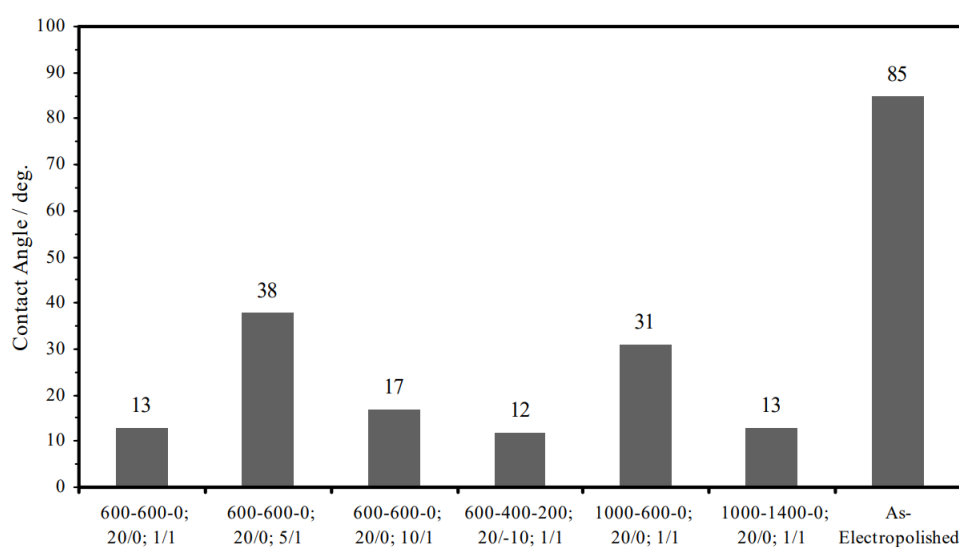


Figure 3.14 : Water contact angles of the anodized samples in comparison to that of as-electropolished sample.

TiO₂ nanotubes were successfully produced on Cp-Ti by the application of bipolar voltage parameters. SEM examinations revealed that morphology of TiO₂ nanotubes are affected by bipolar voltage parameters. When the amplitude of positive pulse increases, nanotube diameter is reduced. The smallest nanotubes diameter was obtained when the amplitude of positive pulse is the highest (1000 μ s). Similarly, increasing neutral period contribute increasing the pore diameter. The highest pore diameter was obtained from the sample oxidized by using the highest neutral period amplitude (1400 μ s). On the other hand, number of successive positive pulses is also effective in determining nanotube morphology. As the number of positive pulses increases, nanotube diameter increases. Finally, when negative voltage is applied to the sample, surface morphology significantly changes from uniform distribution of nanotubes into sponge like random nano structures. Although bipolar voltage parameters affect on surface morphology of the anodized samples, they have no clear effect on the type and intensity of the phases formed at the surface. Anodic oxidation performed in aqueous solution of 1% (vol) HF by using bipolar voltage parameters significantly reduces water contact angle by encouraging a more hydrophilic surface with respect to as-electropolished surface. However there is no systematic correlation between the anodic oxidation parameters and water contact angle values of the surfaces.

3.3.2 Anodic oxidation with pre-deformed foils

Figure 3.15 shows XRD patterns of the samples with different strain levels of uniaxial tension (a) and cold rolling (b). XRD patterns of the samples consist of the representative peaks from diffraction planes of titanium. Upon the comparison of the pre-deformed and undeformed samples, a clear increment was observed at the intensity of 0002 plane of the samples that have been cold rolled. Although an increment in the peak intensity was also obtained for the samples deformed by the uniaxial tension, it was smaller as compared to that in the cold rolled samples.

XRD patterns shown in Figure 3.15 indicate development of preferred orientation upon implementation of strain because there is significant variation in the intensity of (0002) planes. Preferred orientation is obvious for the cold rolled samples in contrast to uniaxial tension samples, whose have minimal changes in their patterns with respect to imposed strain levels. This is a result of the compression deformation induced by

the cold rolling, which mostly affects the basal planes and arranges them to be parallel to the shear plane [62,63]. It suggests that cold rolling is much more effective method to align surface planes to specific orientation as compared to the uniaxial tension strain.

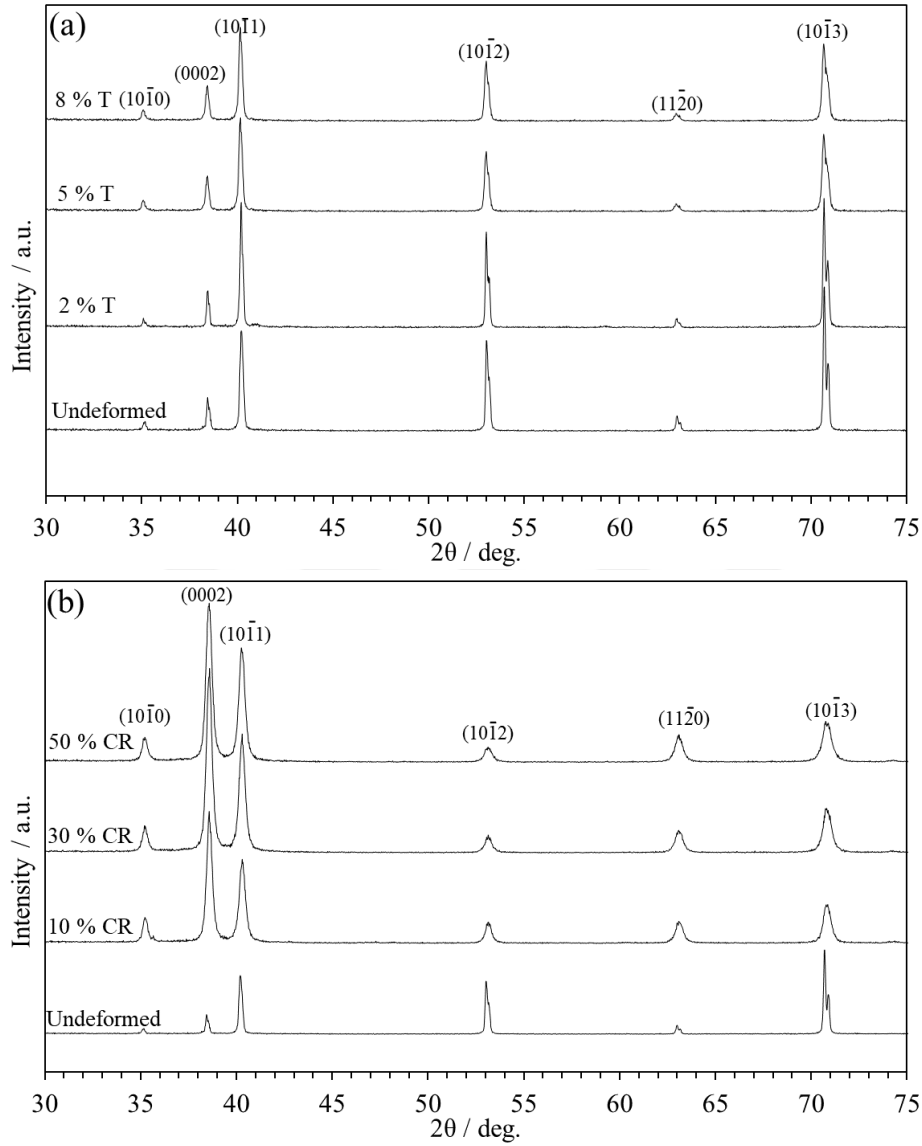


Figure 3.15 : XRD patterns of undeformed and the pre-deformed samples (a) uniaxial tension and (b) cold rolling.

Additionally, microstrain level and crystallite size of the strain induced materials analysed with a whole pattern fitting method namely Williamson-Hall (W-H) method through Eq. 3.4.

$$\beta \times \cos\theta = \frac{K \times \lambda}{D} + 4 \times \epsilon \times \sin\theta \quad (3.4)$$

Where β is full-width half maximum, K is the shape factor (0.9), λ is the wavelength of CuK α radiation (nm), D is average crystallite size (nm) and ϵ is microstrain (%).

W-H plots of the uniaxial tension and cold rolled samples are given in Figure 3.16. In these plots, crystallite size can be estimated as y-intercept value, while microstrain values can be estimated from the slope of the fitted curve. Details of the W-H method is given elsewhere [64,65]. Calculated crystallite sizes and microstrain of the samples are given in Table 3.1. Microstrain is inversely proportional to the crystallite size, and generally increases with increasing deformation amount for both deformation modes. Although the uniaxial tension induced more microstrain than the cold rolling, crystallite size decreased more in the cold rolling than in the uniaxial tension.

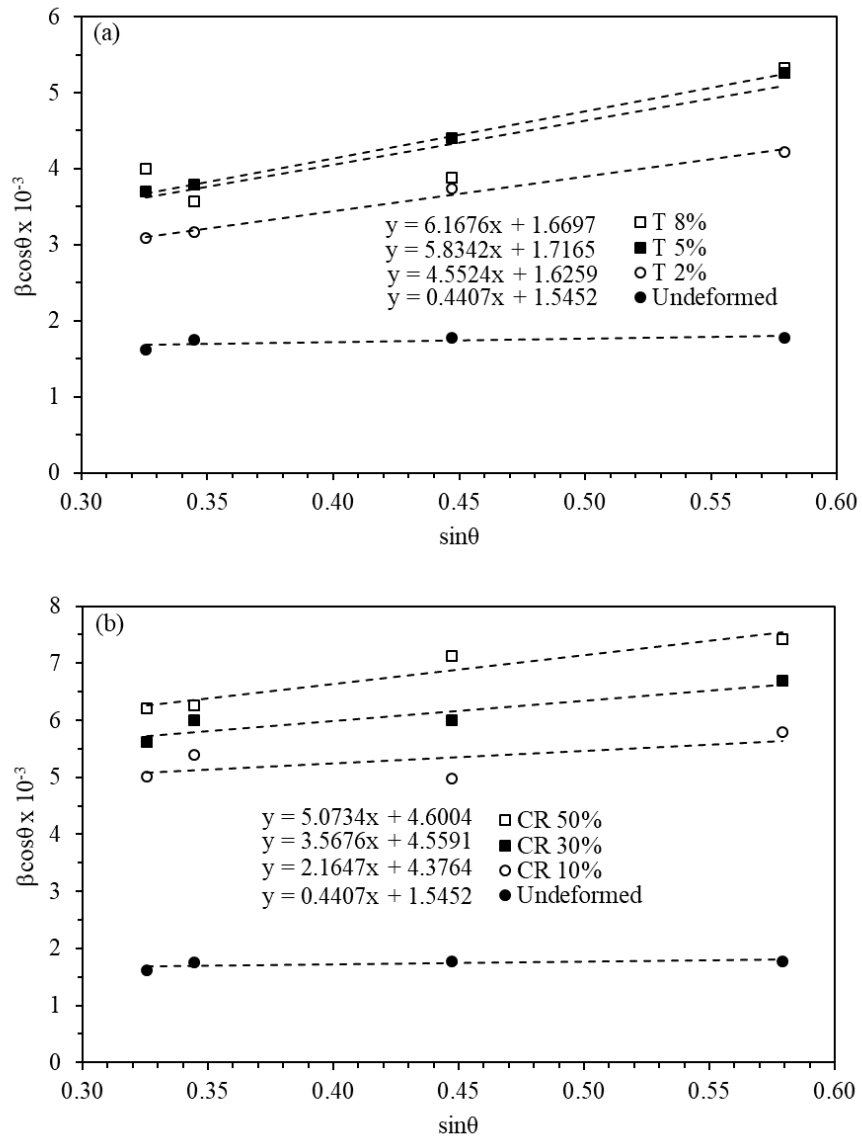


Figure 3.16 : W-H plots of the samples before anodic oxidation for various strain levels in (a) uniaxial tension and (b) cold rolling

Table 3.1 : Crystallite sizes and microstrains of the samples
(T: Uniaxial tension, CR: Cold rolling).

Sample	Crystallite size / nm	Microstrain / %
Undeformed	92.43	0.0100
2 % T	86.66	0.1150
5 % T	81.56	0.1550
8 % T	79.68	0.1450
10 % CR	31.51	0.0600
30 % CR	30.41	0.0900
50 % CR	29.89	0.1275

Figure 3.17 shows variation of the current density with time during the anodic oxidation, which can be evaluated in three successive stages. At the first stage, the current density exhibits a sharp decrement within a very short time due to increasing electrical resistance of the thickening oxide layer on the anode surface. Minimum current density within the first stage generally decreases with increasing amount of uniaxial tension and cold rolling. This is attributed to the fact that decrement in the grain and crystallite size enhances oxygen diffusion to titanium and contributes to the oxide thickening in the first stage [66,67]. At the second stage, the current density increases with time due to the increment in the active surface area and ion diffusion, achieved by dissolution of oxide layer and the formation of pores on the solution-oxide interface. At the third stage, the current density reaches to a steady state level due to a balance between the oxide dissolution at solution-oxide interface and the oxide formation at the metal-oxide interface [68]. During the second and third stages, the current density of the tension samples is quite lower than the undeformed samples, and the minimum current density was achieved in the 5% uniaxial tension sample. On the other hand, cold rolled samples generally exhibited almost similar current densities except for 50% cold rolled sample, which has the lowest current density. Since it was previously reported that plastically deformed titanium has a higher electrochemical corrosion resistance than undeformed titanium [62,69], a lower current density is attributed to a lower dissolution rate of the pre-deformed samples in the second and third stages.

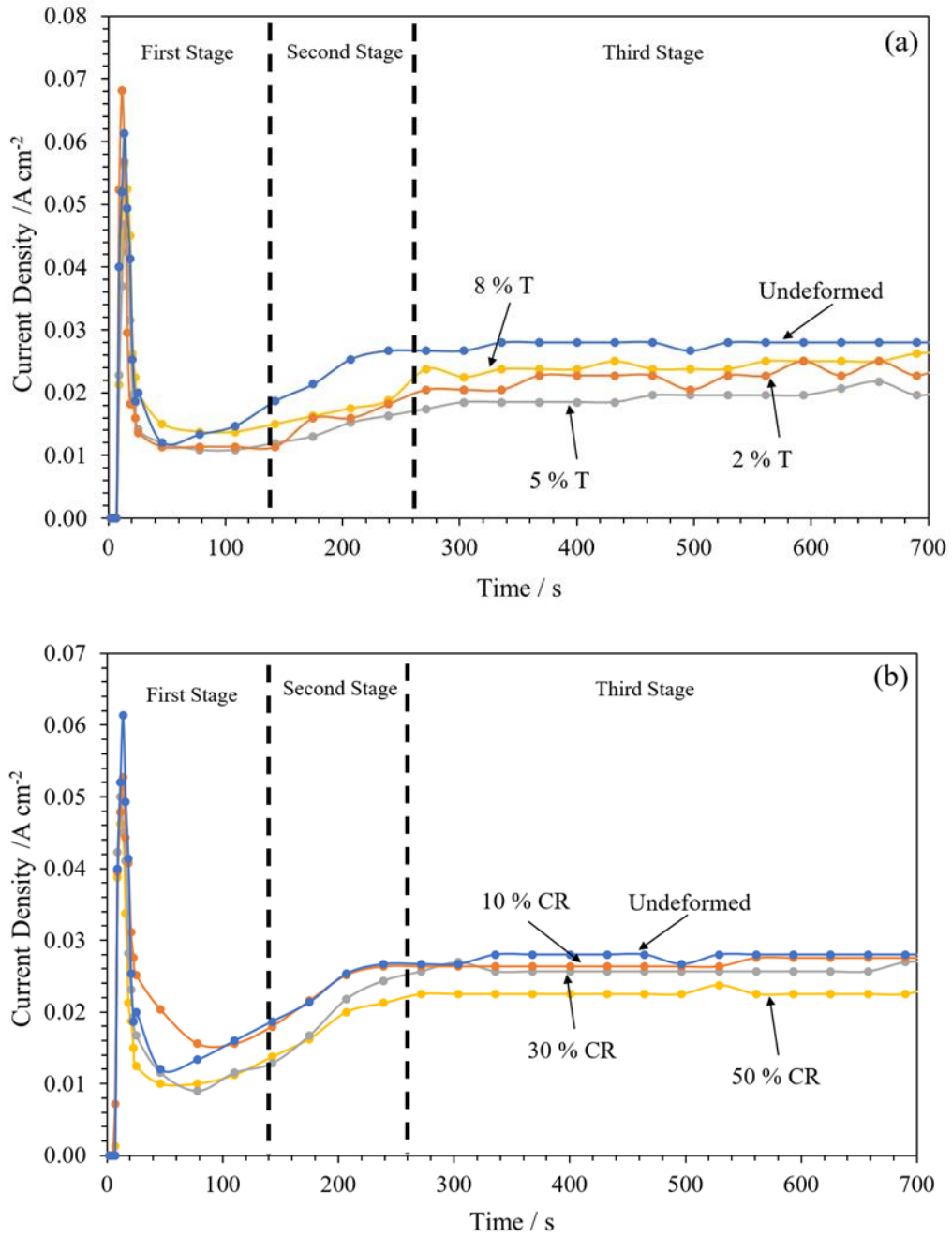


Figure 3.17 : Variation of the current density with time during the anodic oxidation for (a) uniaxial tension and (b) cold rolled samples.

Figure 3.18 shows surface SEM micrographs of the anodized samples. Arrays of nanotube structures are apparent for all samples (Figure 3.18a to 3.18g). Increasing cold rolling strain generally produces more uniform nanotube arrays as evident in Figure 3.18f and 3.18g. On the other hand, amongst the uniaxial tension samples, the best arrays of the nanotubes in terms of uniformity and continuity are obtained from 5% strained sample (Fig. 3.18c). Further increment of tensile strain up to 8% significantly deteriorates the nanotubes morphology, which has either nanotubes free

regions or highly disordered nanotubes (Fig. 3.18d). It is a single exception to increment of uniformity and continuity with increasing strain ratio for the test parameters used in this study. Table 3.2 shows average, minimum and maximum values of the nanotube diameter of the samples with standard deviation. With increasing strain in both deformation mode, average nanotube diameter decreases with a lower standard deviation.

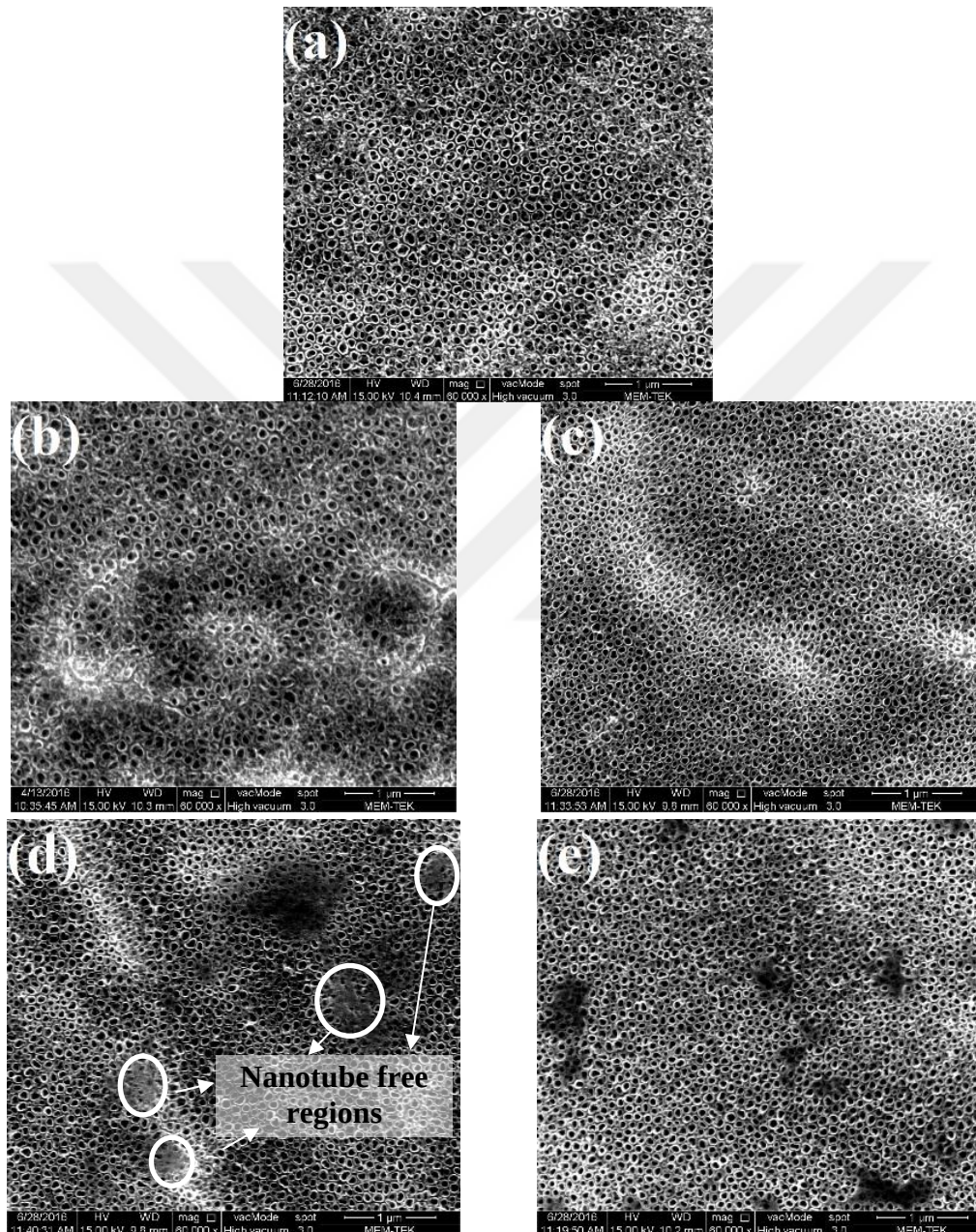


Figure 3.18 : Surface SEM micrographs of the (a) undeformed, (b) 2%, (c) 5%, (d) 8% uniaxial tension and (e) 10% cold rolled samples.

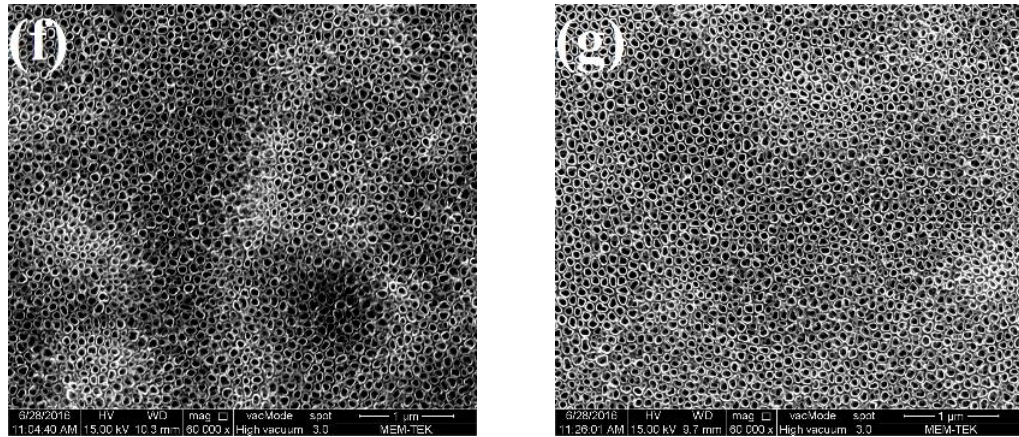


Figure 3.18 (continued): Surface SEM micrographs of the (a) undeformed, (b) 2%, (c) 5%, (d) 8% uniaxial tension and (e) 10% (f), 30% (g) 50% cold rolled samples.

Table 3.2 : Average nanotube diameter of undeformed and pre-deformed samples.

Sample	Nanotubes diameter / nm		
	Min	Max	Average
Undeformed	71	134	101±17
2 % T	73	125	100±18
5 % T	59	88	72±8
8 % T	48	102	72±14
10 % CR	65	108	89±11
30 % CR	58	87	74±10
50 % CR	56	83	70±7

Crystallite size and microstrain level of the samples altered with respect to imposed strain level during uniaxial tension and cold rolling. Microstrain, which is defined as the nonuniform variation of interplanar spacing due to local distortions within the lattice, can affect various chemical and mechanical properties of metals such as corrosion resistance, fatigue strength and hardness [70]. Considering the SEM micrographs in Figure 3.18 and nanotube diameters in Table 3.2, preferred surface orientation and increased microstrain have an effect on the size and the uniformity of the nanotubes produced by the anodic oxidation. It was reported that grains having the orientation of close packed basal planes such as (0002) are the most ideal planes for producing uniform and well-arranged nanotube structures [63]. Thus cold rolling which implements increasing amount of surface orientation with increasing strain, results in a higher uniformity nanotube array upon the application of anodic oxidation process. On the other hand, the variation of the nanotube diameters can be related to

the increasing microstrain induced by decreasing crystallite due to deformation. Smaller crystallite sizes with higher microstrains offer more nucleation sites for oxide film to grow [71].

Figure 3.19 shows the diffuse absorption spectra of the anodic oxidized samples. All samples regardless of the deformation mode show strong absorbance in UV region (below 350 nm) and very low absorbance in the visible region (380-700 nm) and the intensity of absorbance varies with the strain level. While the intrinsic band gap absorption of TiO_2 can be attributed to the major absorbance below 350 nm, physical reasons such as scattering of the light by pores and cracks in the nanotube structure are the reason of the absorption in the visible region [72,73]. Uniaxial tension samples have an increasing absorbance with the strain up to 5%, however further strain (8%) resulted in a significant decrement (Figure 3.19a) in the absorbance. On the other hand, cold rolled samples have a systematic increment in the absorbance with increasing strain level (Figure 3.19b). Cold rolled samples also show better absorption values at both UV and visible ranges when compared to the uniaxial tension samples (Figure 3.19c).

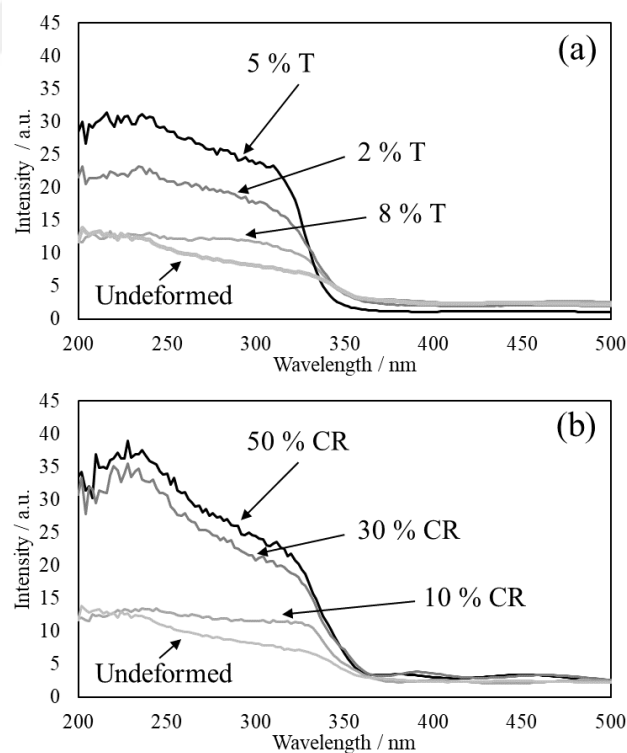


Figure 3.19 : UV-Vis absorption spectra of the (a) uniaxial tension, (b) cold rolled samples and (c) comparison of the samples exhibiting the highest intensity in uniaxial tension and cold rolling.

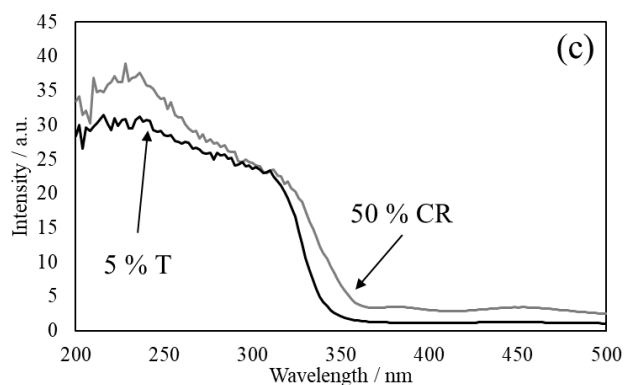


Figure 3.19 (continued): UV-Vis absorption spectra of the (a) uniaxial tension, (b) cold rolled samples and (c) comparison of the samples exhibiting the highest intensity in uniaxial tension and cold rolling.

Diffuse reflectance test indicates photon absorbance potential of the samples in terms of absorption intensity with respect to the wavelength, which shows the excitable charge carriers in the unit area. Thus, increase in the absorption intensity shows the presence of higher amount of photogenerated carriers, which would lead to increased photocatalytic activity. In this context, the observed increments of the photocatalytic performance of the deformed samples can be correlated with the morphological features observed by SEM examinations (Figure 3.18). Since increasing tension strain up to 5% (Figure 3.18a) and cold rolling up to 50% (Figure 3.18b) increased nanotube uniformity and decreased nanotube diameter, higher absorbance is attributed to more uniform nanotubes array and a higher active surface area resulting from a lower nanotube diameter [73].

Figure 3.20 shows photoluminescence spectra of the anodic oxidized samples subjected to cold rolling prior to the anodic oxidation. All of the samples have broad peaks at around 380 nm and small peaks at around 400, 450 and 480 nm. The first peak corresponds to the extinction of excitons, while the others are attributed to the defects and oxygen vacancies on the surface [74]. Intensities of these peaks decreased with increasing strain level. For a semiconductor material such as TiO_2 nanostructures fabricated in the present study, PL emissions are a result of recombination of photo-generated electrons and holes [44,54,75]. The rate of recombination determines the level of photocatalytic efficiency. Decrement of electron-hole recombination rate corresponding to a decrement in the photoluminescence intensity indicates a higher photocatalytic activity.

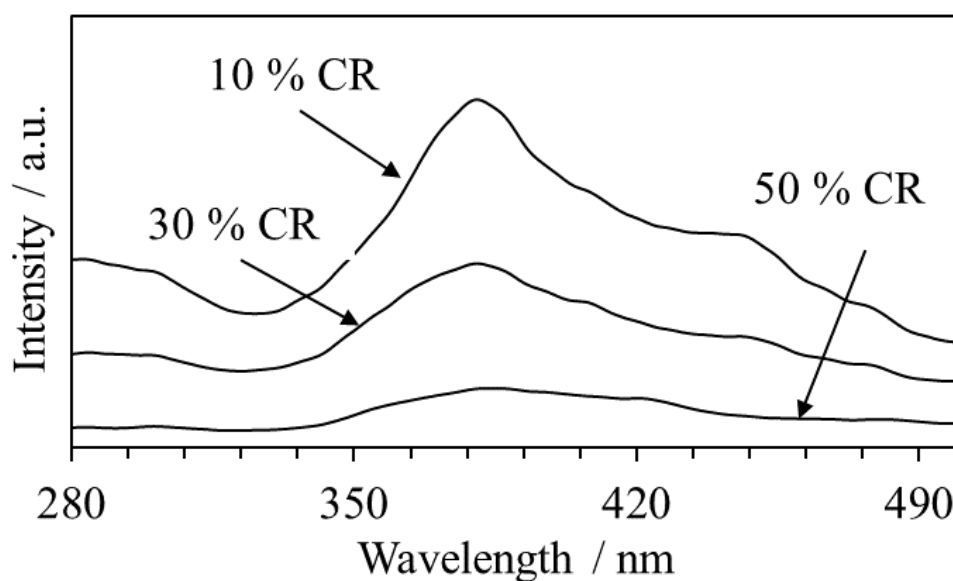


Figure 3.20 : Photoluminescence spectra cold rolled samples.

During photoluminescence test, the semiconductor is excited by high energy photons, and the emission of different wavelength photons with time is monitored. Intensity of photoluminescence occurs as a result of the recombination of photogenerated electron and holes. Since the recombination obstructs photocatalytic activity of these carriers, higher amount of recombination reduces the photocatalytic activity of the material. High level of defects such as microstrains can modify the energy levels of the semiconductor by affecting absorption band edge [76]. It is thus clear that increasing microstrain and decreasing crystallite size accompanied by a higher uniformity of nanotubes are responsible to achieve lower rate of electron-hole recombination, and in turn enhanced photocatalytic activity [77,78].

Figure 3.21 shows the variation of MB concentration (C/C_0) with irradiation time for uniaxial tension (Figure 3.21a) and cold rolled (Figure 3.21b) samples. Degradation rate of MB increases with increasing tensile strain up to 5%, beyond which it is deteriorated with further strain. On the other hand, it continuously increases with increasing strain of cold rolling. The highest photo degradation rate was obtained from the 5% uniaxial tension and 50% cold rolled samples among their groups.

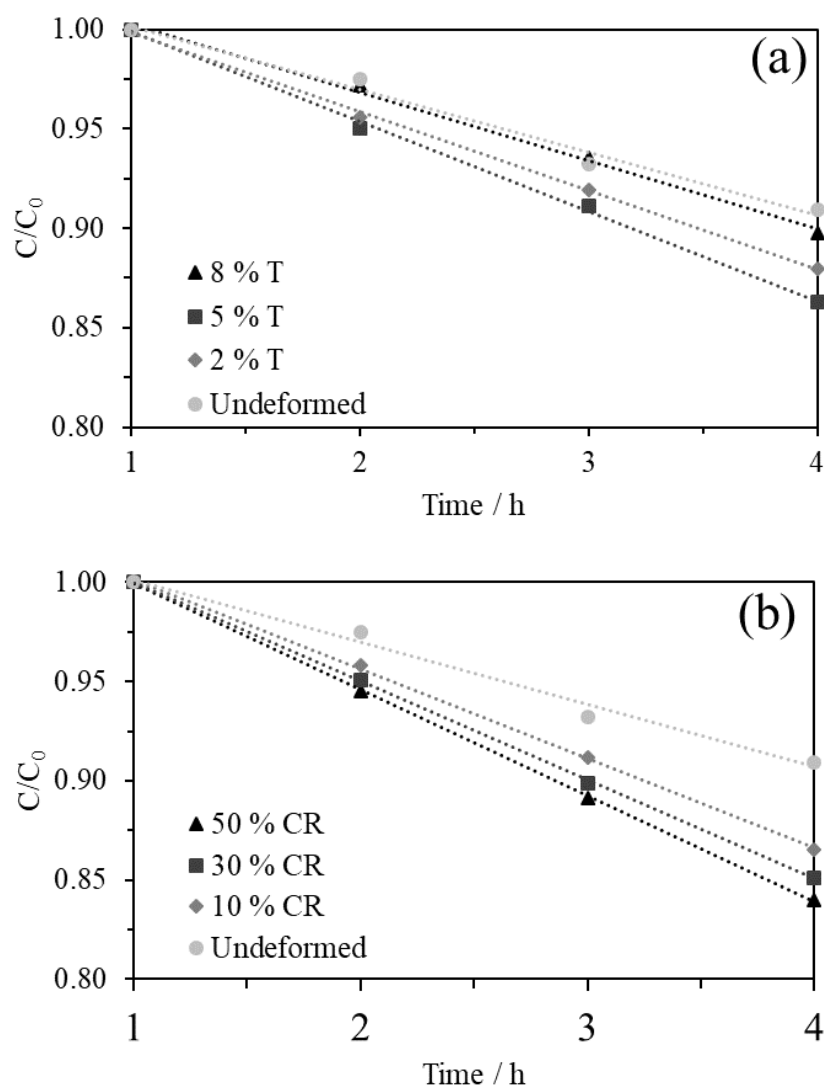


Figure 3.21 : Photodegradation rate of MB with exposure time for undeformed and pre-deformed samples (a) uniaxial tension, (b) cold rolling.

MB degradation tests show the ability of photocatalyst to mineralize organic contaminants. As a very common pollutant MB can be mineralized with redox reactions occurring on the surface of photocatalyst under certain circumstances. For an exposure time of 4 h, it was shown that there was an increment in the MB degradation rate with tension strain up to 5 % and cold rolling up to 50%. Since higher photon absorption capacity and lower charge carrier recombination rate obtained with increasing strain level, degradation of organic pollutant became easier. Thus TiO_2 nanostructures produced on deformed titanium foils up to a certain level showed better degradation properties. In this context, MB degradation test results are compatible with PL and DRS analyses and clearly indicates that pre-deformation applied prior to the

anodic oxidation has a significant effect on the photocatalytic activities of the TiO₂ nanotubes.

3.3.3 Anodic oxidation with carbon structure added electrolytes

In three sequential stages, as shown in Figure 3.22, the current densities change over time during anodic oxidation trials which is a typical pattern of anodic film growth [68]. Due to the growing oxide layer on the anode surface creating electrical resistance, the current density at the first stage displays a significant decrease over a very short period of time. Among the trials with MWCNT, minimum current density within the first stage increased with increment at MWCNT concentration in the electrolyte. MWCNTs in dispersion known to increase conductivity of electrolyte, and they can also increase the conductivity of surface they are attached to by enhancing ion transport [79,80]. Thus, it is clear that MWCNTs could lower electrical resistivity by easing the passing of current through the growing oxide layer. In the second stage, nano pores form on the solution-oxide interface, increasing the active surface area and allowing higher ion diffusion, which causes the current density to grow over time. And at the third stage, balance occurs between oxide dissolution at the solution-oxide interface and the oxide formation at the metal-oxide interface, resulting in steady-state current density [68,81]. During third stage, the current density of the MWCNT samples are higher than reference sample and current density of 0.035 g/L sample is quite higher than the other samples. First reasons for this increment in current density could be increased oxygen evolution reaction (OER) with the presence of MWCNTs on the anode surface. MWCNTs are an efficient OER catalysts [82]. Second reason could be increased oxide dissolution rate at solution-oxide interface however this would comply with continues increase at current density rather than increased level of stable current density. For the 0.035 g/L and reference sample current density is quite stable in third stage, however for the 0.025 g/L and 0.030 g/L samples there are continues increment trend in current density in third stage. Thus, increment in current density for MWCNT samples can be attributed to mainly to OER for 0.035 g/L sample, and increment at oxide dissolution rate for 0.030 g/L and 0.025 g/L samples. This is an important difference since OER, which increase the current density in anodic oxidation process, competes with anodic oxidation of titanium and could lead to formation of non-uniform oxide layer [83]. On the other hand, increment at the oxide dissolution rate could increase pore diameter and vertical growth rate of the tube walls which would

be beneficial for photocatalytic activity due to increment of the active surface area [68].

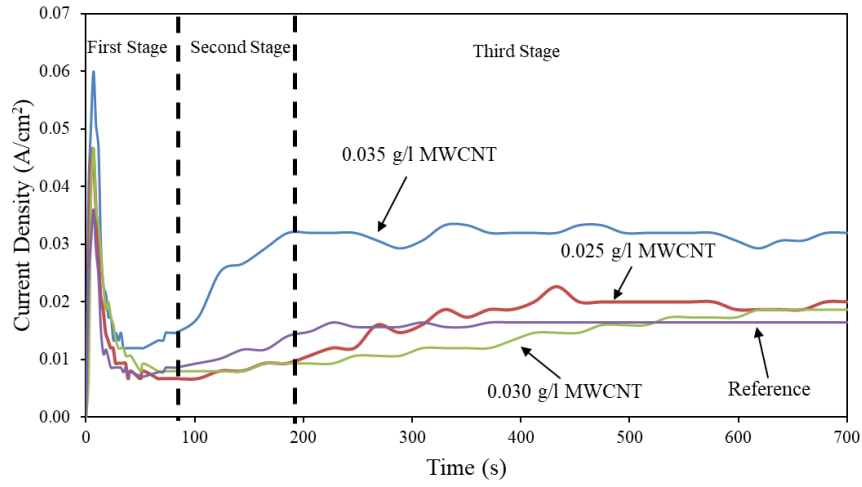


Figure 3.22 : Variation of the current density with time during the anodic oxidation of reference and MWCNT samples.

Figure 3.23 shows surface SEM micrographs of the anodic oxidized samples. For all samples, there are visible arrays of TiO₂ nanotube structures (Figure 3.23a to 3.23d). Also, there are clustered MWCNTs on TiO₂ nanotubes on MWCNT samples (Figure 3.23b to 3.23d). Since CNTs have negative zeta potential even at highly acidic electrolytes such as one that used in this study [84], movement of the negatively charged CNTs to positively charged anode was possible. On the other hand, with the increment at the concentration of the MWCNTs in electrolyte, clustering and covering up of the TiO₂ nanotube surfaces also increased. One other structure observed in micrographs of MWCNTs samples was micropores given in inlets at Figure 3.23c and 3.23d. Since such structures are not observed in reference sample, occurrence of this pores is attributed to the presence of MWCNT clusters at the surface. Possible reason for the formation of these micropores is local electrical discharges caused by increased electrical conductivity of the anode surface by clusters of MWCNTs. Since, when the applied electric field is greater than the dielectric strength of the oxide layer, conductive channels begin to form through the oxide layer by electrochemical breakdown leading to the creation of micropores in the oxide layer [85]. Even though higher voltages compared to those used in this study are needed for the dielectric breakdown of oxide films, increased local current density caused by clustered MWCNTs could lead to these pores, particularly if there are defects or irregularities in the oxide layer, such as nanotubes formed by anodic oxidation.

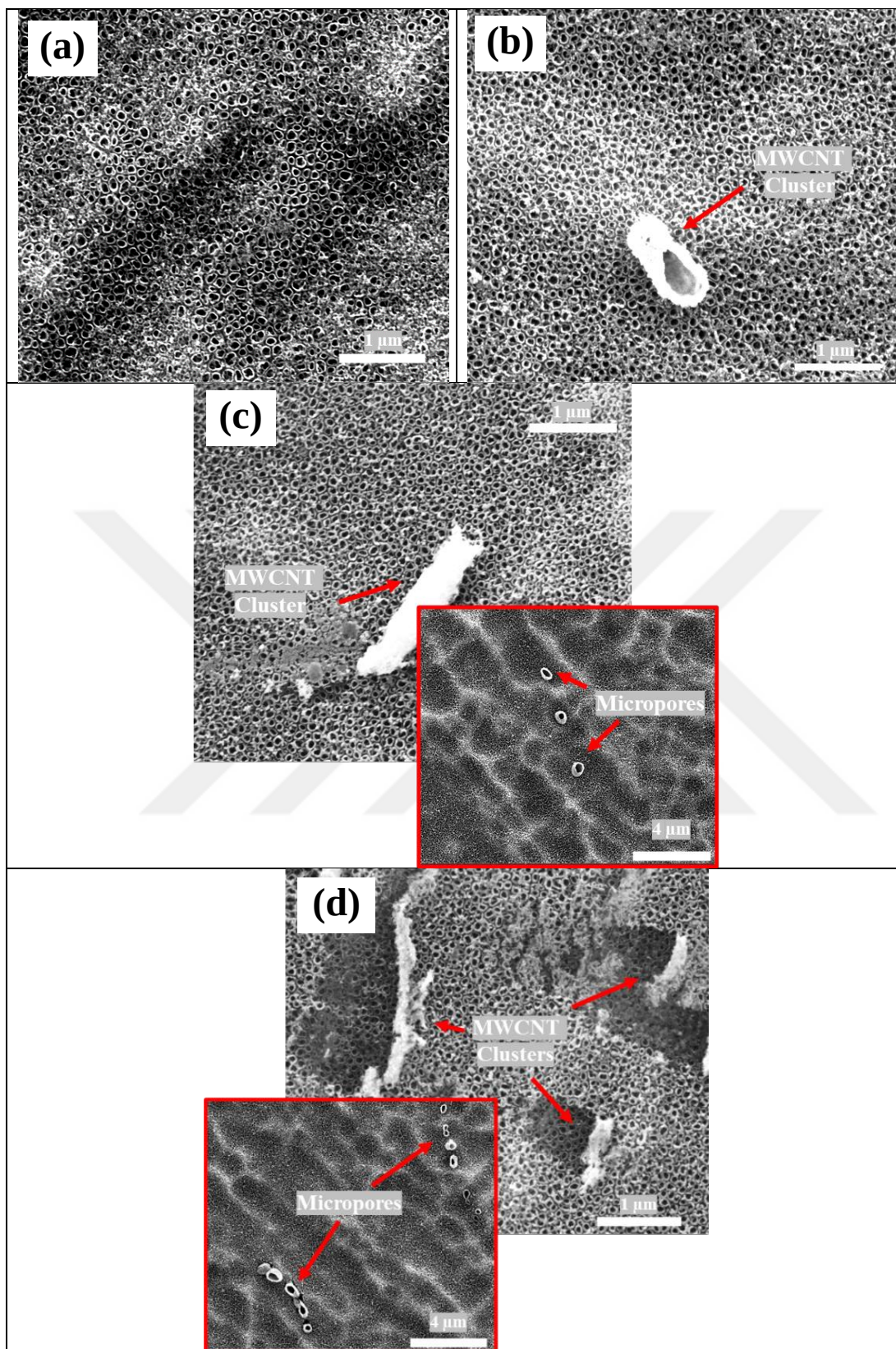


Figure 3.23 : Surface SEM micrographs of the (a) reference (0 g/L MWCNT), (b) 0.025 g/L MWCNT, (c) 0.030 g/L MWCNT and (d) 0.035 g/L MWCNT sample.

Figure 3.24 shows Raman spectra of MWNCT samples after annealing. Peaks at 150, 398, 519 and 641 cm^{-1} are assigned respectively to the E_g , B_{1g} , A_{1g} and E_g modes of crystalline anatase phase with a slight blue shift at every peak. Raman shifts are primarily associated with surface lattice strain states, and blue shifts are attributed to the compression strain, which leads to the increased frequency of phonons interacting with the incident photon [75,86]. This is an indication for the higher photocatalytic activity of MWNCT samples since they have a higher potential to use incident photons. For MWCNT samples, in addition to the anatase peaks there are also two carbon peaks at 1350 and 1586 cm^{-1} which are respectively assigned to D and G bands of MWCNTs. The first one is common for disordered carbon and indicates mainly defects in structure like vacancies and tube edges as well as additional carbon-based impurities, and latter one is characteristic for graphite structure that is highly aligned [87]. Thus, raman analyses verify successful deposition and the presence of MWCNTs on the TiO_2 nanotubes.

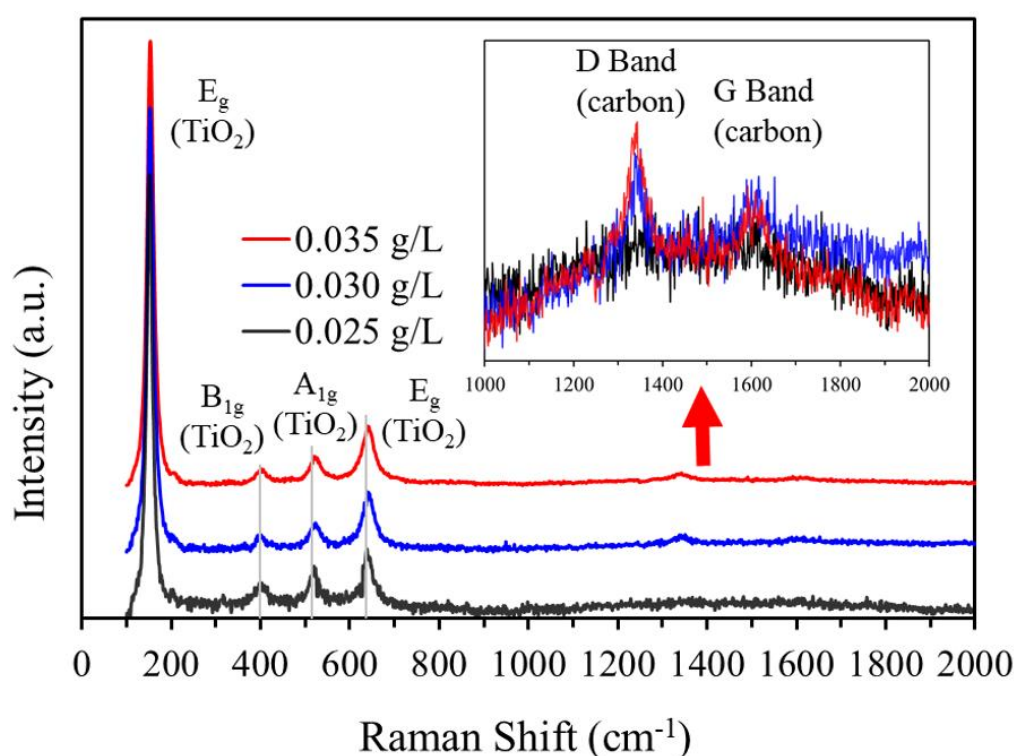


Figure 3.24 : Raman spectra of the samples anodic oxidized in MWCNT added electrolytes

Figure 3.25 shows the absorption spectra of the reference and MWCNT samples. All samples exhibit significant UV region absorbance (below 350 nm) and very low visible

region absorbance (380–700 nm), with MWCNT concentration influencing the strength of absorption. While the main cause of absorbance below 350 nm can be attributed to the intrinsic band gap absorption of TiO_2 , the absorption in the visible region is caused by physical factors including light scattering from pores and cracks in the nanotube structure [72,73]. Diffuse reflectance testing shows the photon absorbance potential of the samples in terms of absorption intensity in relation to wavelength, and as the intensity increases, the absorbance and utilization potential of photons also increases. All of the MWCNT samples show higher absorbance intensity than the reference sample, and it increases with decreasing MWCNT composition. CNTs know to have light suppression and trapping ability [88–90] which would explain increased absorption at MWCNT samples compared to reference sample. On the other hand, increased deposition and clustering of MWCNTs as observed in SEM micrographs would be the reason for decreasing absorption with increasing MWCNT concentration. These heterogenous carbon structures could cover the surface and block the absorption of light to the underlying TiO_2 nanotube structure [38,91].

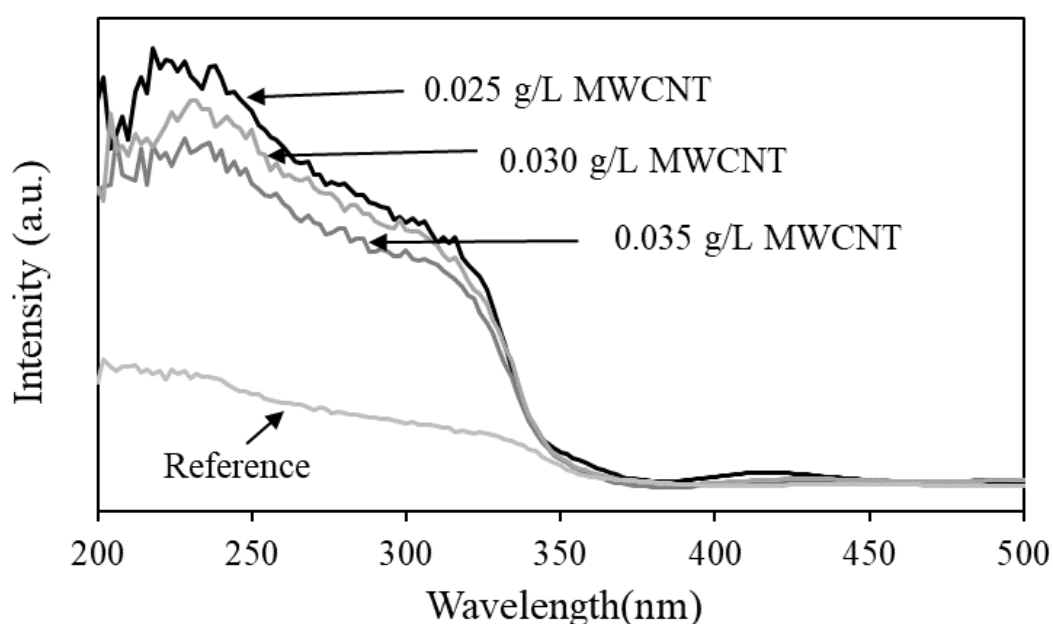


Figure 3.25 : UV-Vis absorption spectra of the reference sample and samples anodic oxidized in MWCNT added electrolytes.

Figure 3.26 shows photoluminescence spectra of all samples. There are large peaks in all of the samples at around 380 nm and smaller peaks at 430 and 470 nm. While the first peak is related to the extinction of excitons, the surface flaws and oxygen vacancies are responsible for the other peaks [74]. All of the MWCNT samples have

lower peak intensities than the reference sample. Photoluminescence test measures the emission of photons at various wavelengths from a material activated by high energy photons. Photoluminescence intensity is affected by the recombination of photogenerated electrons and holes for a semiconductor material such as TiO_2 , and it increases with increments at recombination [44,54,75,92]. Because recombination obstructs the photocatalytic activity of semiconductors, a higher photoluminescence intensity corresponds to lower photocatalytic activity. It is well documented that CNTs can act as electron scavengers by taking photogenerated electrons from the conduction band of TiO_2 . In the absence of CNTs, these electrons would recombine with holes in the valance band of TiO_2 created by excitation by photons [92–94]. Thus, it clear that the MWCNTs deposited on to the TiO_2 nanotubes lowered the recombination rate of e-h pairs and improved photocatalytic performance. On the other hand, there is no clear correlation between photoluminescence intensity and MWCNT concentration as 0.025 g/L sample showing highest and 0.030 g/L showing lowest intensity values among MWCNT samples. Decrement at the photoluminescence intensity with increment at MWCNT concentration is expected, however non uniform oxide layer and higher amount of micropores as observed in SEM micrographs could be the main reason for lower performance of 0.035 g/L sample.

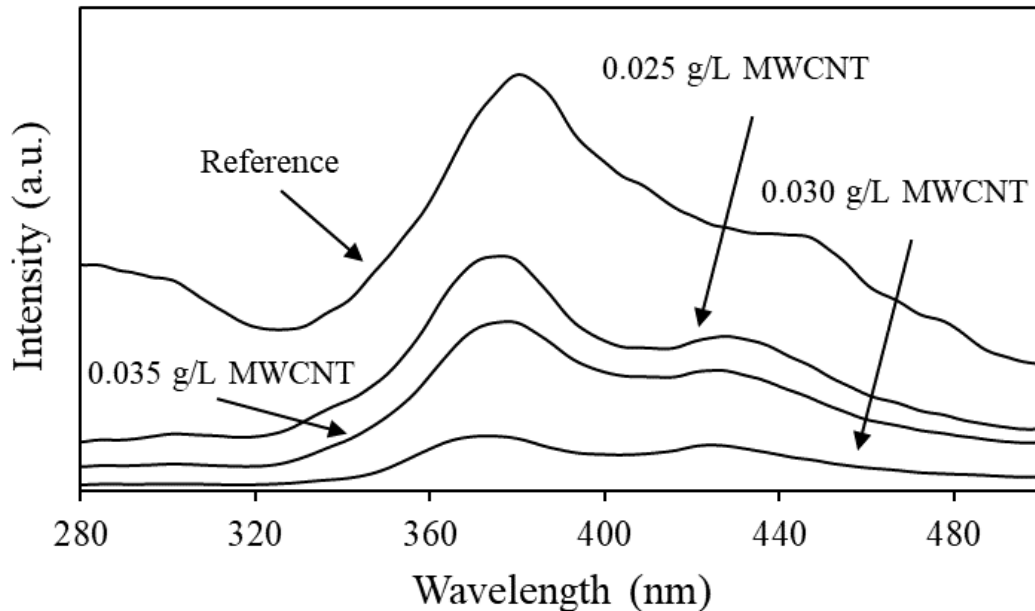


Figure 3.26 : Photoluminescence spectra of the references sample and samples anodic oxidized in MWCNT added electrolytes.

Figure 3.27 shows the variation of MB concentration (C/C_0) with irradiation time for all samples. All of the MWCNT samples have a higher degradation rate of MB compared to the reference sample, and as the MWCNT concentration increases, the degradation rate decreases. The ability of a photocatalyst to mineralize organic pollutants is demonstrated by MB degradation experiments. MB known as a very common and a model pollutant and can be mineralized with redox reactions occurring on the surface of a photocatalyst [48,95]. Rate of degradation highly depends on the photocatalytic performance of photocatalyst. Thus, MB degradation test results are compatible with PL and DRS analyses and clearly indicates that deposition of MWCNTs on the TiO_2 nanotubes have a noteworthy positive effect on photocatalytic performance of TiO_2 nanotubes. Since higher photon absorption capacities and lower e-h recombination rates obtained with deposition of MWCNTs, degradation of organic pollutant became easier. However, as the MWCNT concentration increases degradation ability of composite surface decreases.

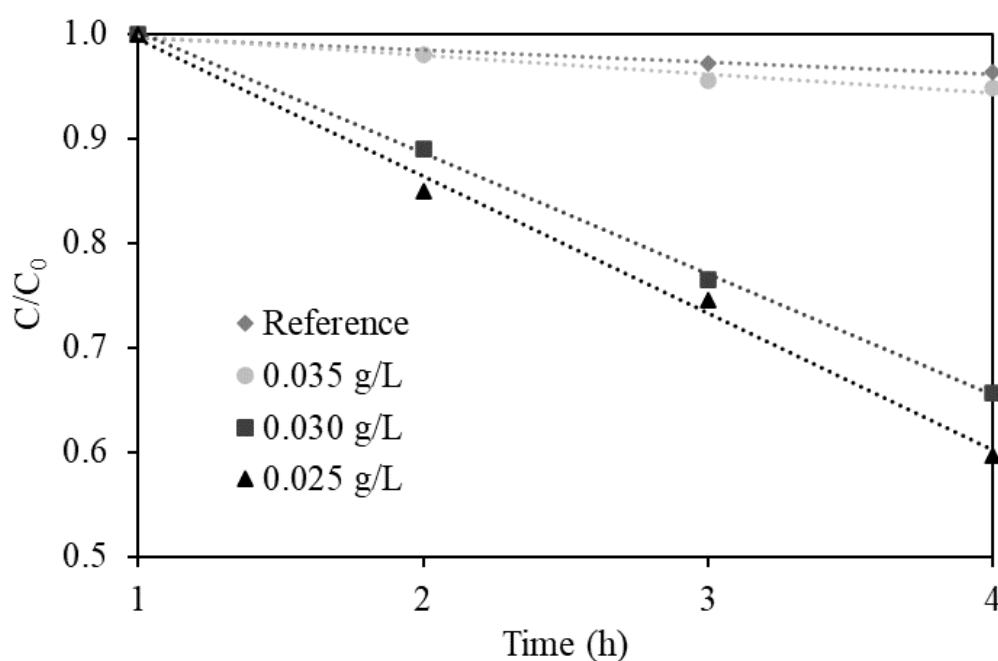


Figure 3.27 : Photodegradation rate of MB with exposure time for reference sample and samples anodic oxidized in MWCNT added electrolytes.

6. CONCLUSIONS AND RECOMMENDATIONS

Following an investigation into the impacts of several parameters, such as applied voltage, processing time, electrolyte agitation, and electrolyte temperature during the electropolishing of Cp-Ti in an alcohol-based electrolyte, the following results were reached. By doing the electropolishing for a shorter period of time at a higher voltage, satisfactory surface finishes can be obtained both at a low applied voltage (35 V) and at a high applied voltage (75 V). At a specific applied voltage, electropolishing that is too short or too long does not produce a surface quality that is suitable. The ideal processing time at a specific applied voltage results in the best electropolishing in terms of smoothening and brightness. This period is 8 minutes at 35 volts, 3 minutes at 65 volts, and 2 minutes at 75 volts. After electropolishing, a surface with poor surface quality always has an oxide coating on it. To get rid of the oxide layer and to produce a more even and smooth surface, electrolyte agitation is always required. In alcohol-based electrolytes, a small degree of initial electrolyte temperature increase can speed up the electropolishing process and produce better surface finishes than lower temperature processes. When the procedure is constrained by a brief period of electropolishing (1 minute in this study), better electropolishing outcomes are obtained at a higher temperature (35 °C in this study) than at room temperature.

Study to produce heat resistant and oxidizable titanium and aluminum intermetallic surfaces provided the following results. Process variables distinguished the coating's structure, thickness, and oxidation performance on titanium samples. Coating thickness is increased by raising the temperature of the aluminizing process, controlled cooling following the aluminizing process and preheating before the aluminizing process. Intermetallic phases of TiAl_2 and TiAl_3 have been detected in the generated coatings. Intermetallic phases occur more steadily at lower aluminizing process temperatures than at higher process temperatures. With all process variables, titanium's oxidation resistance has significantly increased. Compared to higher temperature, lower temperature aluminizing result in coatings that are more oxidation resistant. The

final coating's oxidation resistance is increased by preheating samples before the aluminizing process.

Bipolar voltage parameters were successfully used to manufacture TiO₂ nanotubes on Cp-Ti. Bipolar voltage factors have an impact on the morphology of TiO₂ nanotubes, according to SEM analyses. The diameter of the nanotube decreases as the positive pulse's amplitude rises. Similar to this, a longer neutral period increases pore diameter. On the other hand, the quantity of succeeding positive pulses can also be used to analyze the shape of nanotubes. The diameter of the nanotube rises with the amount of positive pulses. Finally, the surface morphology of the sample drastically changes from a uniform distribution of nanotubes to random nanostructures that resemble sponges when negative voltage is supplied to the sample. Although bipolar voltage settings have an impact on the anodized samples' surface morphology, they have no discernible impact on the kind and quantity of the surface phases. Bipolar voltage parameters are used for anodic oxidation in aqueous solution containing 1% (vol) HF, dramatically lowers the water contact angle by promoting a more hydrophilic surface compared to the electropolished surface. However, there is no consistent relationship between the surface water contact angle values and the anodic oxidation parameters.

Effects of the deformation on the produced nano structures investigated and following result are determined. Cold rolling and uniaxial tension both improve the near surface (0002) planes' preferred orientation. Cold rolling, however, produces more potent (0002) peaks and is hence more efficient than uniaxial tension. Regardless of the deformation mode, crystallite size decreases during deformation. However, compared to uniaxial stress, cold rolling significantly reduces crystallite size. The size of the crystallites is continuously reduced by cold rolling and increasing tensile strain. The relationship between microstrains and crystallite size is inverse. Uniaxial tension produces higher microstrains than cold rolling despite having a smaller applied strain. Uniaxial tension and cold rolling (up to 5% tensile strain and 50% cold rolling) lower the size of the nanotubes while improving their homogeneity. Photocatalytic activity of the nanotubes increases with increasing strain up to 50% in cold rolling and up to 5% strain in uniaxial tension.

Simple way for deposition of MWCNTs on TiO₂ nanotubes with anodic oxidation of CP-Ti foils demonstrated. However, as no auxiliary agent used in electrolytes for better dispersion of MWCNTs, clustering of MWCNTs on TiO₂ nanotube surface observed.

And with the increment at the MWCNT concentration, clustering and covering up of TiO₂ nanotube structures also increased. In terms of photocatalytic performance, samples produced with MWCNT including electrolytes showed higher light absorption and lower charge recombination rates, which reflected to the MB degradation tests with better degradation performance. 0.025 g/L MWCNT sample, which is the lowest MWCNT concentration used in this study, showed the best photocatalytic performance and with the increment at MWCNT concentration photocatalytic performance deteriorated rapidly. The main reason for this was determined to be increased surface covering causing, lower light absorption potential, and increased production of micropores during anodic oxidation due to clustering of MWCNTs.





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