

**SURFACE TREATMENT OF Ti-6Al-4V ALLOY BY
THERMAL OXIDATION**

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**M.Sc. Thesis by
Hasan GÜLERYÜZ, B.Sc.**

(706011003)

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Supervisor (Chairman): Prof. Dr. Hüseyin ÇİMENÖĞLU

[Signature]

Members of the Examining Committee: Prof.Dr. E. Sabri KAYALI (İTÜ)

S. Kayali

Prof.Dr. Mehmet DEMİRKOL(İTÜ)

[Signature]

**YÜKSEKÖĞRETİM KURULU
DENEYİM MERKEZİ**

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**Ti-6Al-4V ALAŞIMININ YÜZEY ÖZELLİKLERİNİN
TERMAL OKSİDASYON İLE GELİŞTİRİLMESİ**

**YÜKSEK LİSANS TEZİ
Met. Müh. Hasan GÜLERYÜZ**

(706011003)

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Tezin Savunulduğu Tarih : 30 May 2003

Tez Danışmanı : Prof. Dr. Hüseyin ÇİMENÖĞLU

Diğer Jüri Üyeleri : Prof.Dr. E. Sabri KAYALI (İTÜ)

Prof.Dr. Mehmet DEMİRKOL (İTÜ)

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FOREWORD

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ABBREVIATIONS

CP	: Commercial Purity
HCP	: Hexagonal Close Packed
BCC	: Body Centered Cubic
PVD	: Physical Vapor Deposition
CVD	: Chemical Vapor Deposition
XRD	: X-Ray Diffraction
GXRD	: Glancing Incidence X-ray Diffraction.
PMMA	: Polymethylmethacrylate
UHMWPE	: Ultrahigh Molecular Weight Polyethylene
ODZ	: Oxygen Diffusion Zone
3-D	: Three Dimensional



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LIST OF SYMBOLS

k	: Oxidation rate constant
h	: Oxide thickness
z	: Diffusion depth
C	: Concentration
D	: Diffusion coefficient
t	: Time
T	: Temperature
Q_o	: Activation energy of oxidation
Q_d	: Activation energy of diffusion
R	: Gas constant
H	: Hardness
A	: Indentation contact area
σ_r	: Residual stress
P_{ave}	: Average contact pressure
θ	: Temperature compensated time parameter

Ti-6Al-4V ALAŞIMININ YÜZEY ÖZELLİKLERİNİN TERMAL OKSİDASYON İLE GELİŞTİRİLMESİ

ÖZET

Titanyum alaşımları üstün özellikleri sayesinde, medikal aygıtları da içeren çeşitli uygulama alanlarında kullanılmaktadır. Fakat uzun süreli ve etkin kullanımları yetersiz tribolojik özellikleri nedeniyle kısıtlanmaktadır. Ti-6Al-4V alaşımı mekanik özelliklerinin yanısıra hafifliği ve korozyon direnci ile, özellikle ortopedik implant uygulamaları için tercih edilen bir malzeme olmasına rağmen uygulama sürecinde aşınma etkisi ile oluşan parçacıklar implantı çevreleyen dokunun tepki vermesine neden olur ve implantın kısa bir süre sonrasında değiştirilmesini gerektirir.

Titanyum alaşımlarının medikal uygulamalar için vazgeçilmez olması, yetersiz aşınma özelliklerinin yüzey işlemleri ile geliştirilmesini gerekli kılmaktadır. Termal oksidasyon yöntemi ile görece kalın TiO_2 ve yüzeyden içeri doğru gelişen oksijen difüzyon tabakası elde edilmektedir. Basitliği ve uygulama kolaylığının yanısıra sağladığı yüzey özellikleri ile iyileştirilmiş korozyon direnci ve aşınma performansı sağlamaktadır.

Bu çalışmada, soğuk işlem görmüş Ti-6Al-4V alaşımının termal oksidasyon koşulları araştırılmıştır. Kütlesel sertlikten fedakarlık yapmadan, mekanik olarak kararlı ve korozyona dirençli yüzey tabakası oluşturan oksidasyon koşullarının belirlenmesi amaçlanıldığından, bu oksidasyon koşullarında işlem gören alaşımın aşınma ve korozyonlu aşınma davranışları değerlendirilmiştir. Yüzey tabakasının karakterizasyonu mikroskopik incelemeler, ultramikrosertlik ölçümleri ve X-ışını difraksiyon analizi ile gerçekleştirilmiştir. Farklı işlem koşulları sonucu elde edilen yüzeylerin görece korozyon direnci 5 M HCl çözeltisinde test edilmiştir. Buna göre 600°C'de 60 saat oksidasyon sonucu elde edilen yüzeyin korozyona karşı en fazla direnci gösterdiği belirlenmiştir. Aşınma testleri kayma aşınması durumunu temsil eden aşınma cihazında gerçekleştirilmiştir. Kuru ve % 0,9 NaCl içeren ortamlarda gerçekleştirilen deneylerinde 600°C'de 60 saat yapılan oksidasyon ile aşınma direncini aşırı miktarda arttığı görülmüştür. % 0.9 NaCl içeren çözeltide gerçekleştirilen aşınma deneylerinde yüzey işlemi uygulanmamış alaşıma nazaran oksidasyon sonrası aşınma direnci 25 kat artmıştır.

SURFACE TREATMENT OF Ti-6Al-4V ALLOY BY THERMAL OXIDATION

SUMMARY

Although titanium alloys present excellent properties for various applications, including medical devices, their poor tribological performance limits their long-term efficiency in human body. The well-known Ti-6Al-4V alloy is a favorable material especially for orthopedic implants which provides the combination of desired mechanical properties such as high yield strength, fatigue strength and fracture toughness in conjunction with low weight and good corrosion properties. However, detrimental effects of wear induced particle release and eventual adverse tissue reactions results with the need of revision surgery in short term after implantation.

It is a matter of concern to improve the wear properties of titanium alloys by means of surface engineering, since they are the most appropriate materials for biomedical applications. Thermal oxidation is a simple way of producing wear resistant surfaces for titanium alloys. By utilizing the suitable treatment condition, modified surface layer, which is composed of TiO_2 and oxygen diffusion zone, provides enhanced corrosion and wear properties for titanium alloys.

In this study, comparative investigation of thermal oxidation treatment for cold worked Ti-6Al-4V was carried out. Since the aim was to form a mechanically stable and corrosion resistant surface without sacrificing the bulk hardness, the optimum oxidation conditions were determined for further evaluation of wear and corrosion wear performance. Characterization of modified surface layers were carried out by means of microscopic examinations, ultramicrohardness tests and X-ray diffraction analysis. Relative corrosion resistance of untreated and oxidized samples revealed by accelerated corrosion tests in a solution of 5M HCl. The examined Ti-6Al-4V alloy exhibited excellent resistance to corrosion after oxidation at 600°C for 60 hours. Wear tests were conducted on a reciprocating wear tester in dry sliding condition and in a 0.9 % NaCl solution. Oxidation of Ti-6Al-4V alloy at 600°C for 60 hours improved both dry sliding and corrosion wear resistance, significantly. In 0.9 % NaCl solution, oxidized alloy exhibited 25 times higher wear resistance than the untreated alloy.

1. INTRODUCTION

Titanium and titanium alloys have two principal virtues: A high strength to weight ratio and a good corrosion resistance. It can be strengthened greatly by alloying, heat treatment and deformation processes. Interest in the properties of titanium and its alloys began to accelerate with aerospace applications and became more and more widely recognized. At one time or another all aerospace structures (airframes, skins and engine components) have benefited from the introduction of titanium. Non aerospace applications are medical devices, steam-turbine blades, nuclear and fossil fuel power generation plants, off-shore marine constructions, the pulp-and-paper industry and the chemical industry [1,2].

The earliest applications of titanium as a material for medical, surgical and dental devices were based on the advances in titanium manufacturing processes for aerospace and military requirements. The commercial purity (CP) titanium grades and Ti-6Al-4V were first titanium biomaterials introduced in implantable components and devices. As device manufacturers investigated the potential advantages of titanium, new devices and improved versions of older devices were created that utilized the properties of titanium. This stimulated the need for better understanding of biological response to titanium alloys and initiated research into improved properties for the requirements of dental applications, total joint replacement systems, medical fasteners and fracture fixation devices [3].

Modern surgery and dentistry need metals and alloys of extreme chemical inertness and adequate mechanical strength. Metals and alloys, besides titanium, for biomedical use; are stainless steels, Co-Ni-Cr alloy, cast and wrought Co-Cr-Mo alloy. CP titanium is a material of choice as an implant because of its biocompatibility resulting in no allergic reaction with the surrounding tissue. If a higher strength of the implant is necessary, for example, in hip prostheses, titanium alloys have to be used. The most widely used alloy, Ti-6Al-4V, reaches a yield strength almost double the yield strength of CP titanium. Prostheses fabricated from

wrought Ti-6Al-4V show almost double the load bearing capacity when compared to cast cobalt alloys [4].

In contrast to their superior mechanical properties and biocompatibility that make them superior candidates for implants, titanium alloys are characterized by poor tribological performance, including high and unstable friction coefficients, severe adhesive wear and susceptibility to fretting wear. A better understanding of their tribological behavior and enhancement in wear resistance should be achieved [5,6].

Although pure titanium is highly reactive metal it is usually protected by the presence of a very stable, self-healing passive oxide film consisting mainly of TiO_2 . It is this film is responsible for affording titanium and its alloys with excellent corrosion resistance, in many aqueous media, and assures their excellent biocompatibility [7]. The use of titanium alloys, especially Ti-6Al-4V, as bearing surfaces in total human joint replacements, like artificial hip joints, was widespread during the 1970s. However, following revision surgery, after several years use, concerns were raised regarding the creation of unwanted wear debris. Such debris are produced as a result of combined actions of corrosion and wear (corrosion-wear). It is very important to consider the synergy between corrosion and wear; because wear is increased by the action of corrosion and corrosion increased by the action of wear [7,8].

Poor tribological behavior of titanium alloys due to their inherent characteristics can be improved by means of surface engineering [1,4,9,10]. Many techniques including PVD coatings, thermal spray coatings, ion implantation, thermochemical diffusion (N, C, B, O) treatments were proposed to enhance wear resistance [1]. Among these treatments diffusion processes, especially oxygen diffusion hardening, are more promising because of the fact that sufficient resistance of underlying base material to plastic deformation is required for mechanical integrity of the surface layer during rubbing contact [6].

Thermal oxidation of titanium and titanium alloys results in the formation of an exterior oxide layer and inner oxygen diffusion zone. Relatively thicker oxide layer enhances corrosion resistance. Dissolution of oxygen at the surface increases hardness due to interstitial solid solution formation [1,5,9,10,11].

In conclusion, a simple treatment based on high temperature oxidation can significantly improve corrosion-wear performance of titanium alloys where it has a crucial importance for biomedical applications.

In the present study thermal oxidation of a cold worked Ti-6Al-4V alloy has been examined to find out the optimum oxidation parameters to form a mechanically stable and corrosion resistant surface layer, without sacrificing the bulk hardness.



2. PHYSICAL METALLURGY OF TITANIUM

2.1. Processing of Titanium

Titanium is an allotropic element that, it exists in more than one crystallographic form. At room temperature, titanium has an hexagonal close-packed structure (hcp), which is referred to as “ α ” phase. This structure transforms to a body-centered cubic (bcc) at 883 °C, which is named as “ β ” phase.

The extraction of titanium metal from the ore involves a carbo-chlorination process, which converts titanium oxide to titanium tetrachloride. The most common method of titanium reduction is Kroll process, which is the reaction of TiCl_4 with liquid magnesium at high temperatures. The resultant product of reduction process is titanium sponge. Later it is purified by crushing into small particles and then acid leaching or vacuum distillation to produce commercially pure (%99.0) titanium.

Titanium alloys are produced by mixing the titanium sponge with various metallic elements such as aluminum, vanadium, iron, tin, niobium, molybdenum, chromium and zirconium to produce a wide range of titanium alloys with varying physical, chemical and mechanical properties. Titanium sponge, alloying elements and clean recycled scrap chips are mechanically compacted by cold pressing into compacts which are used as feed stock for consumable-electrode vacuum-arc process. Melting in vacuum reduces the hydrogen content of titanium alloys and essentially removes other volatiles. This tends to result in high purity cast ingot [1-3].

Primary fabrication of titanium include all operations that convert ingot into mill products-billet, bar, plate, sheet, strip, extrusions, tube and wire. Secondary fabrication refers to manufacturing processes such as die forging, extrusion, hot and cold forming, machining and joining, all of which are used for producing finished parts from mill products [2].

More commonly, following heat treatments are considered to achieve the desired property combinations [2];

- Stress relief annealing to reduce residual stresses developed during fabrication,
- Mill or process annealing to produce an acceptable combination of strength, ductility, machinability, dimensional stability with suitable microstructure,
- Solution treatment and aging to increase strength.
- Heat treatments to optimize mechanical properties such as fracture toughness, fatigue strength and high temperature creep resistance.

2.2. Classification of Titanium Alloys

The α phase (hcp) of titanium is found at low temperatures, where β phase (bcc) is stable at elevated temperatures. High temperature β phase can be maintained at low temperatures by alloying. Alloying elements can be classified as α or β stabilizers. α stabilizers, such as aluminum and oxygen, increase the temperature at which α phase is stable. β stabilizers, such as vanadium and molybdenum, result in stability of the β phase at lower temperatures.

Generally, the microstructural features can be categorized as; α microstructure, $\alpha + \beta$ microstructure and β microstructure. However, following specific microstructural constituents may be observed [1];

- Primary α is the room temperature hcp phase that persists during heat treatment at the α - β phase field,
- Secondary α is, namely transformed β refers to α structures that arise during cooling through subtransus region or annealing below the transus temperature,
- α_2 (Ti_3Al) forms during aging treatment if the oxygen concentration is above 0,2 wt.% and the aluminum concentration is higher than the solubility limit (6 wt.%),
- Martensitic microstructures may form, if the cooling rate from the β field is sufficiently rapid,

- Equilibrium β structure may be present at room temperature due to partitioning of alloying elements at high α - β phase field and subsequent slow cooling,
- Metastable β can be retained at room temperature; if an alloy with sufficient β stabilizers is cooled rapidly enough from high in the α - β phase or from above the β transus.

Various room temperature microstructures of typical α - β alloy Ti-6Al-4V upon cooling can be seen in Figure 2.1.

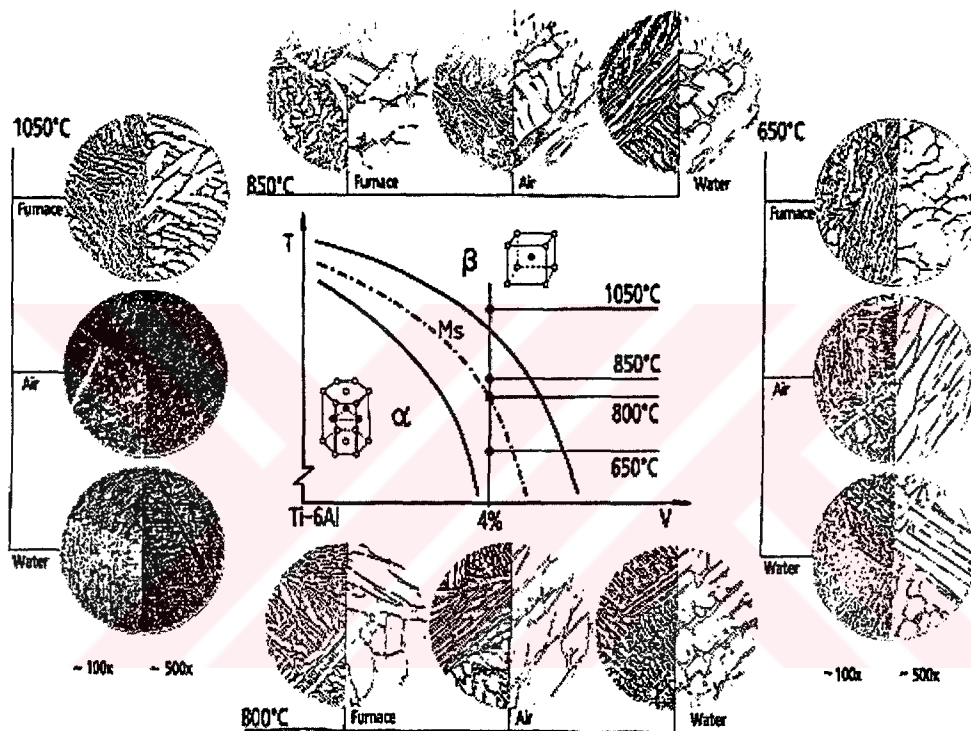


Figure 2.1. Various microstructures of Ti-6Al-4V upon cooling from different temperatures [1].

2.3. Microstructure - Mechanical Property Relationship in Titanium Alloys

The effects of microstructure on the various properties of titanium alloys are schematically shown in Figure 2.2.

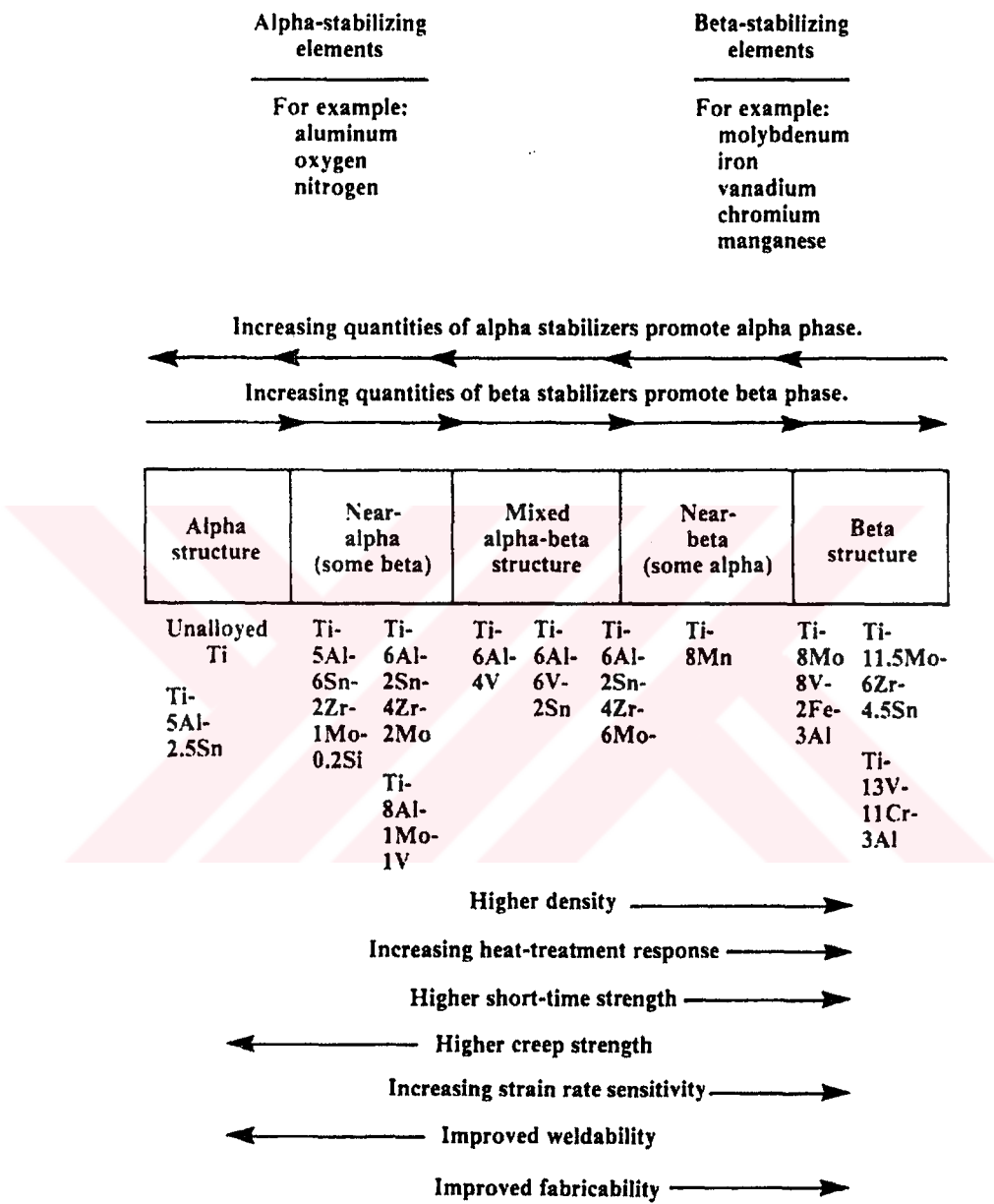


Figure 2.2. Effects of alloying elements on titanium alloy structure and properties [2].

These microstructural features of the titanium alloys significantly affect the mechanical properties depending on the alloy composition and the thermal-mechanical processing history. Therefore, microstructure of titanium alloys may be customized to achieve certain mechanical properties. Certain heat treatments and

deformation processes results in combination of several microstructural features and upgraded mechanical properties. Mechanical properties of common titanium alloys can be seen in Table 2.1. Effects of individual structures on mechanical properties are summarized in Table 2.2.

Table 2.1. Mechanical properties of common titanium alloys [2].

Designation	Tensile strength, MPa	Yield strength, Mpa	Elongation, %	Reduction in area, %	Hardness, Rockwell	Alloy type
Ti CP-2	345	276	20	30	80 HRB	α
Ti CP-4	552	483	15	25	100 HRB	α
Ti-5Al-2,5Sn	690	586	15	25	24 HRC	α
Ti-6Al-4V	931	862	15	30	36 HRC	α - β
Ti-6Al-7Nb	862	793	10	25	32 HRC	α - β
Ti-13Nb-13Zr	860	725	8	15		β
Ti-12Mo-6Zr-2Fe	1000	965	15	40	33 HRC	β

Table 2.2 Relationship between selected microstructural features and mechanical properties of titanium alloys [1].

FEATURE	ENHANCES	DEGRADES
Equiaxed primary α	• Strength • Ductility • Fatigue initiation resistance • Low cycle fatigue resistance	• Fracture toughness • Fatigue crack growth resistance • Notched fatigue resistance
Elongated primary α	• Fracture toughness • Fatigue crack growth resistance • Notched fatigue resistance	• Ductility • Fatigue initiation resistance • Low cycle fatigue resistance
Secondary α	• Strength • Ductility	• Fracture toughness
α_2 (Ti ₃ Al)	• Strength	• Fracture toughness
Coarse prior β grains	• Fracture toughness • Creep	• Strength • Ductility • Low cycle fatigue resistance • Fatigue initiation resistance
Fine prior β grains	• Strength • Ductility • Fatigue initiation resistance	• Fracture toughness • Notched fatigue resistance

3. CORROSION AND WEAR OF TITANIUM ALLOYS

3.1. Corrosion of Titanium Alloys

Titanium and its alloys with their outstanding mechanical properties and high strength to weight ratio, also offer excellent corrosion properties. As far as corrosion is concerned, they belong to large group of oxide-passivated metals including stainless steels and nickel, cobalt, aluminum-based alloys. Titanium in its various grades and alloys is used in a wide variety of aerospace, marine, and chemical and biomedical applications because it is largely immune to corrosion related failure in most environments [2,3].

The excellent corrosion resistance of titanium alloys results from the formation of a very stable, continuous, highly adherent and protective film on the surface. Surface oxide film forms instantly when fresh metal surface is exposed to air and/or moisture. In fact, a damaged oxide film can generally reheal itself instantaneously if at least traces of oxygen or water are present in the environment [2,12].

Recognizing that the corrosion resistance can be described only for a defined material/medium system, some fundamental difficulties arise in practice. Materials differ with regard to their chemical composition, impurities, structure and surface condition. On the medium side, it is not only the type and concentration of chemical ingredients, but also physical and mechanical parameters such as temperature, pressure, stress, friction and wear [1,2].

Titanium and its alloys exhibit excellent resistance to atmospheric corrosion in both marine and industrial environments. However, if titanium is exposed to strongly oxidizing or reducing environments (high temperature air exposure or hot, concentrated acid environment), severe corrosion is observed [1,12].

The nature, composition and the thickness of the protective surface oxides that form on titanium alloys depend on environmental conditions. In most aqueous environments, the oxide is TiO_2 , Ti_2O_3 or TiO . High temperature oxidation tends to promote the formation of chemically resistant, crystalline form of TiO_2 known as

rutile, whereas lower temperatures often generate the more amorphous form of TiO_2 , anatase or a mixture of rutile and anatase. The TiO_2 oxide is generally chemically resistant and is attacked by very few substances, including hot, concentrated HCl , H_2SO_4 , NaOH , H_3PO_4 and HF [1,12].

Bloyce et al. reported that thick oxide layer produced on commercially pure titanium by high temperature oxidation provided excellent corrosion resistance in boiling 10% HCl solution for 18 hours test duration where as polished samples continually dissolved and lost weight [13].

3.2. Wear of Titanium Alloys

Although titanium alloys offer attractive mechanical and physical properties, their application is limited where friction and wear is a matter of concern. Inherent characteristics of titanium cause strong adhesion to counter material during sliding contact that gives rise to high and unstable friction coefficients.

Poor tribological behavior of titanium alloys is related to their electron configuration, crystal structure and lubrication ineffectiveness [1,4,8]. Electron configuration of titanium possesses a low value of d-bond character. This situation leads to extreme reactivity of titanium surface. Although most of the metals having hcp structure exhibit good frictional properties, titanium is distinguished from the others. The crystal structure of titanium differs from other hexagonal metals with a low axial ratio of 1.588, which is less than ideal close packed structure with a ratio of 1.633. This situation tends to make the basal plane less favorable to slip and allows prismatic and pyramidal slip planes to operate. Increased number of operational slip systems enhances ductility and promotes plastic deformation at the asperity junctions leading to higher friction during sliding contact. Another factor that affects the frictional properties of titanium is the poor response to lubrication. It has been reported that all conventional lubricants (mineral oils and greases), which are successfully and widely used for most metals, have been shown to be ineffective when applied to titanium alloys. Additionally, the low heat conductive nature of titanium adds to the problem of ineffectiveness of lubricants. As a result of inherent material properties, titanium alloys are very susceptible to adhesive and abrasive wear. High reactivity of the surface and deformation behavior of the subsurface regions cause severe damage and material transfer to mating surface [4,8,14].

Ductility and chemical reactivity of titanium alloys enhance plastic deformation and adhesion at the real contact area that is maintained on the asperity junctions. This in turn induces high values of friction coefficient for titanium alloy mating either itself or another counter material. Moreover, adhesion strength of junctions is usually much higher than strength of titanium alloy and such junctions eventually rupture within the titanium asperities, which accounts for many craters on the worn surface. Ruptured particles may transfer to counter material or form small wear debris. After multiple contacts in the wear couple work hardening of wear debris or transferred titanium develops and results in severe abrasive damage to titanium surface [4].

Long and Rack [14] studied reciprocating-sliding wear of several titanium alloys against maraging steel with a hardness of 58 HRC. They reported that the worn surfaces of the alloys under investigation exhibited extensive plastic deformation, micro-plowing, micro-cracking perpendicular to the sliding direction, shear delamination and smearing, accompanied by heavy transfer to counterpart and mechanical alloying with the counterpart.

Dong and Bell [15] investigated the wear of Al_2O_3 balls sliding against Ti-6Al-4V and a hardened AISI 52100 steel. They found that the wear coefficient of Al_2O_3 is about three orders of magnitude higher when sliding against Ti-6Al-4V disc than against hardened steel disc under the same conditions. Based on the results of wear debris analysis, they postulated the wear mechanism with respect to tribochemical reactions due to high reactivity and low thermal conductivity of titanium alloy.

Titanium and titanium alloys are considered to have poor oxidative wear resistance when tribochemical reactions occur at contact area. Atmospheric oxygen radically changes the friction coefficients and wear rates during dry sliding wear. High sliding speed induces temperature increase at the contact area and cause uncontrollable oxidation of the surface. This leads to generation of oxide wear debris and increased wear rate. In addition to surface characteristics, the mechanisms involved in the friction and wear of titanium alloys require particular attention on the subsurface deformation induced during wear. High-strain deformation in the near-surface zone of a material undergoing wear is a fundamental part of the wear process [6].

Molinari et al.[16] investigated the dry sliding wear mechanism of Ti-6Al-4V alloy mating itself. They described the wear mechanism as oxidative wear of a plastically

strained surface. The results they found confirmed the low resistance to plastic deformation of the alloy even at low loads. Poor protection of the surface oxide was due to the mechanical instability of the surface layers caused by plastic deformation.

3.3. Corrosion - Wear of Titanium Alloys

Corrosion is often related to a number of factors of mechanical, thermal and chemical origin acting simultaneously. There is a clear need for a better understanding of the mechanism behind the collective influence of environmental degradation factors on titanium alloys, particularly in situation where chemical, electrochemical wear act simultaneously [3].

As mentioned earlier, corrosion performance of titanium alloys is based on the passive oxide layer that easily forms in oxidizing mediums. This oxide layer assures their durability in use. However, continuous removal of the oxide layer due to sustained wear action threatens the long-term stability of titanium surfaces. Hence, on determination of tribological properties, combined action of corrosion and wear should be taken into account. This realizes the simultaneous effects of corrosion and wear, namely the corrosion-wear performance [2,7].

The surface chemical reactions, which are beneficial in preventing adhesive wear will, if unchecked, lead to considerable loss of underlying material. If a metal is corroded to produce a film on its surface while it is simultaneously subjected to a sliding contact then one of the following processes may occur [17,18];

- A durable lubricating film which inhibits both corrosion and wear may be formed,
- A weak film may be produced and a high rate of wear may occur due to regular formation and destruction of the film,
- The protective films may be worn and a galvanic coupling between the remaining films and the underlying substrate may result in rapid corrosion,
- The corrosion and wear processes may act independently to cause a material loss and sum of the two processes added together.

The high corrosion-wear rate of titanium alloys is related to mechanical instability of the oxide layer. It is proposed that when normal and shear stresses are high enough to

induce the breakdown of the surface passive layer, the oxide will be disrupted. The exposed metal surface may then either reform a passive layer or adhesively bond to the counter material. This situation leads to continuous removal (material disruption) and reformation (oxidation) of the passivating layer and results in gradual consumption of the alloy material. Concurrently, breakdown of the oxide layer creates the potential for abrasive wear, where the hard oxide debris act as third body abrasive components [6].

Galliano et al. [19] investigated the simultaneous effects of corrosion and wear by conducting sliding wear tests in 0,9 % NaCl solution. Experimental setup allowed monitoring the electrochemical parameters during wear testing. They measured that the onset of rubbing led to sharp increase in anodic current and the formation of a galvanic couple between the wear track (anode) and the outside surface (cathode), which decreased the corrosion potential to provide an enhanced corrosion rate.

Komotori et al. [7] studied the effect of prior abrasion damage on corrosion of surface treated titanium alloys. They observed the greater dissolution of untreated alloys due to large extent of abrasion damage.

4. SURFACE MODIFICATION TREATMENTS FOR TITANIUM ALLOYS

Poor wear resistance of titanium alloys requires the use of surface engineering to minimize the wear debris generation. Since increased surface hardness promotes better friction properties and resistance to adhesive and abrasive wear, various procedures including hard coatings, ion implantation and thermochemical treatments may be considered, for this purpose [3,6].

Hard coatings can be applied to titanium and titanium alloys by means of CVD and PVD processes, with a coating thickness of 3-5 μm . However, there are several limiting factors for the use of such coating in practice [1,3,7].

- The risk of failure due to insufficient adhesion of coating and the high stress concentration that may occur at the discontinuity between the hard coating and the titanium substrate,
- Severe localized corrosion due to galvanic coupling of the coating and the substrate maintained through the small defects (micro pores) reaching to substrate,
- High cost of coating process.

Ion implantation of titanium surface with high energy ions changes the composition and properties of the surface. Nitrogen and oxygen are particularly suitable for bombarding ions. Despite the fact that the concentration of the implanted elements is quite low, an increase in hardness of the surface region is noted. However, the maximum penetration depth is low when compared to other surface modification techniques [1,3].

Thermochemical surface treatments offer the advantage of producing deeper hardened surface layer due to thermally induced diffusion of species like carbon, nitrogen and boron at elevated temperatures. These treatments are high temperature processes that cause irreversible grain growth resulting in low mechanical properties. Mechanical properties of titanium alloys are highly dependent on hydrogen

contamination. It is a matter of fact that, these treatments are usually conducted in hydrogen containing atmospheres [1].

Thermal oxidation is a high temperature oxidation treatment of titanium alloys to provide a oxygen-rich case hardened zone and relatively thick oxide layer. This treatment is named as oxygen diffusion hardening. Interstitial solid solution formation, beneath the oxide layer, due to diffusion of oxygen atoms results in increased surface hardness. Depending on the concentration of oxygen, the hardness gradually decreases from surface to the inner regions of the metal. For the sake of processing simplicity and enhanced surface properties such as wear and corrosion, thermal oxidation is the most promising surface treatment for titanium alloys [5-7,9,10,13,20-26].



5. OXIDATION OF TITANIUM AND TITANIUM ALLOYS

5.1. Progress of Oxidation

Titanium is so reactive that it forms oxides when exposed to any oxygen containing species at room temperature. The oxide film, which is generally only a few nanometers thick, forms naturally and protects the underlying, highly reactive titanium metal against uncontrolled further oxidation [3,7].

A variety of different stoichiometries of titanium oxides are known to cover a wide range of oxygen to titanium ratios, such as Ti_3O to Ti_2O , Ti_3O_2 , TiO , Ti_2O_3 , Ti_3O_5 and TiO_2 . The most stable titanium oxide is TiO_2 and exists in three different crystallographic forms: Rutile, anatase with tetragonal and brookite with orthorhombic structure [3].

Oxidation, particularly at temperatures above $200^{\circ}C$, significantly increases the thickness from a few nanometers to several tens of nanometers and changes the structure from amorphous to crystalline of the oxide film [3,13]. Below $1000^{\circ}C$, mostly rutile modification of TiO_2 forms [27].

At elevated temperatures formation of an outer thick oxide scale is accompanied with dissolution of oxygen in the subsurface zone. Titanium may dissolve large amounts of oxygen up to 30 at.% [27,28]. According to Ti-O phase diagram oxygen readily dissolves more in α phase than β phase. Dissolution of oxygen in beta phase, in turn stabilizes alpha phase and shifts the $\alpha + \beta$ transition temperature to higher values. Phase diagram of Ti-O binary system can be seen in Figure 5.1.

In metal lattices, interstitially dissolved atoms may occupy two types of interstitial sites, which have octahedral and tetrahedral symmetry of lattice atoms. Octahedral sites are larger and may accommodate larger atoms like carbon, nitrogen and oxygen [27]. Weissmann and Shrier [29] carried out a strain analysis study on high purity

mechanisms of titanium alloys change both with time and temperature and follows different rate equations [27,31]:

- Logarithmic rate equation: Below 400°C reaction is initially quite rapid and then drops off to low or negligible levels.

$$X = k \log(t + t_o) + C \quad (5.1 \text{ a})$$

- Parabolic rate equation: Reaction rate decreases with time at temperatures above 600-700°C.

$$X^2 = kt + C \quad (5.1 \text{ b})$$

- Linear rate equation: The rate is constant with time above 900-1000°C.

$$X = kt + C \quad (5.1 \text{ c})$$

where X is the measured quantity due to oxidation, k is rate constant of oxidation, C is the integration constant and t is oxidation time, respectively. Schematic illustrations of variation of X with time according to logarithmic rate (Figure 5.2), parabolic rate and linear rate (Figure 5.3) are shown in the figures below.

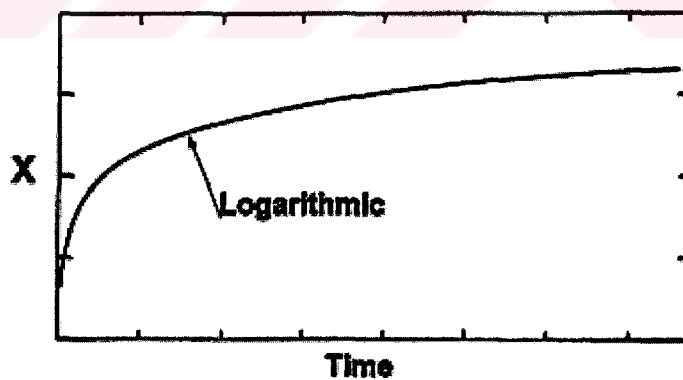


Figure 5.2. Variation of measured quantity X with time during logarithmic oxidation [27].

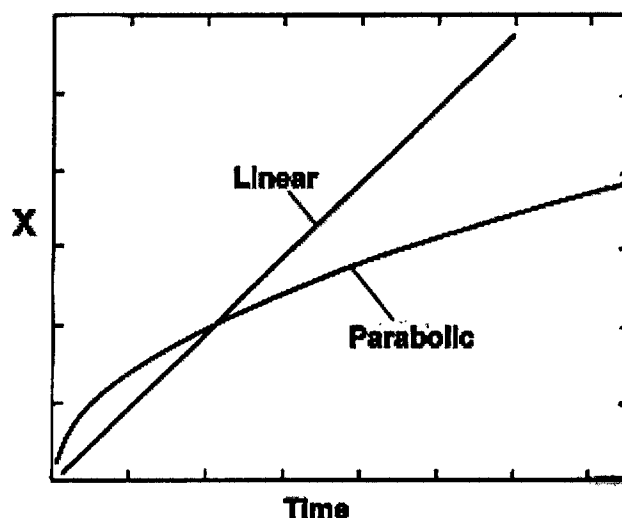


Figure 5.3. Variation of measured quantity X with time during parabolic and linear oxidation [27].

The logarithmic oxidation involves oxide film formation below 400°C. Above 600°C simultaneous oxygen dissolution and oxide scale formation confirms parabolic oxidation. Between 400-600°C a transition occurs between logarithmic and parabolic where dissolution of oxygen becomes more important with increasing temperature. Above 900-1000°C linear oxidation reflects increased rate of oxide formation while oxygen dissolution continues at a rate determined by the oxygen gradient and diffusion coefficient of oxygen in the metal [27].

It is suggested that the parabolic oxidation of titanium is governed by the diffusion of oxygen in both the oxide and the metal core. Oxygen diffuses inwards through the compact oxide and is consumed by oxide growth and oxygen dissolution at the metal oxide interface [27]. Oxygen diffuses beyond the oxide - metal interface into the base metal. This penetration is a result of the oxygen gradient, high solubility of oxygen in titanium and relative ease of interstitial diffusion [32]. Diffusion of oxygen, like other interstitial solute atoms N and C, takes place by the interstitial mechanism in which the solute atoms successively jump from one interstitial site to another.

Weight gain data provides the determination of overall oxidation (oxide formation and oxygen diffusion) kinetics of titanium alloys. According to weight gain measurement, total oxidation kinetics follows parabolic rate law at temperature range 600-800°C [33,34]. Oxide scale, TiO_{2-y} has a small oxygen solubility range that the value of y is approximately 0,01-0,02. On the other hand, there is a steep

concentration gradient in the oxygen solid solution zone [35]. Oxide thickness measurements (h) confirm parabolic oxidation through the Equation 5.2 [33];

$$h^2 = kt \quad (5.2)$$

Temperature dependence of oxidation rate constant (k) can be quantified by the Arrhenius equation [27,35];

$$k = Ae^{(-Q_o / RT)} \quad (5.3)$$

where; A is frequency factor, Q_o activation energy of oxidation, R is gas constant (8,3143 J/mol °K) and T is the absolute oxidation temperature.

Du et al. [34] who studied air oxidation behavior of Ti-6Al-4V alloy between temperature range of 650 - 850°C and calculated Q_o as 267 kJ/mol according to weight gain method. For this material total oxidation activation energy Q_o was reported as 192 kJ/mol, where oxide growth activation energy, which was calculated through Equation 5.2, was quantified as 147 kJ/mol at 600-700°C by Frangini et al. [33]

Unnam et al. [35] investigated the oxidation of commercially pure titanium at temperature range of 593-760°C and they reported the oxide growth activation energy (Equation 5.2) as 114 kJ/mol.(cp ox)

5.3. Kinetics of Oxygen Diffusion

Large oxygen solubility range in the oxygen solid solution zone necessitates the utilization of Fick's second law [35]

$$\frac{C - C_s}{C_o - C_s} = \text{erf}\left(\frac{z}{2\sqrt{Dt}}\right) \quad (5.4)$$

where, C_s is concentration at the metal-oxide interface, C_o is initial concentration in the metal, C is concentration at the distance z from surface, D is diffusion coefficient and t is time.

Solution of Equation 5.4. gives diffusion coefficient of dissolving oxygen at a certain temperature, which later on can be used to find out the diffusion activation energy of oxygen in titanium or titanium alloys (Q_d) [27,35].

$$D = D_o e^{(-Q_d / RT)} \quad (5.5)$$

where, D_o is diffusion constant.

Oxygen diffusion kinetics can be determined by various methods. X-ray diffraction analysis, strain ageing, internal friction and microhardness measurements are used to investigate the diffusion kinetics [27,36]. Since linear relation between the microhardness of the material and the concentration of the dissolved oxygen is established, Equation. 5.4 can be rewritten as

$$\frac{H - H_s}{H_o - H_s} = \text{erf}\left(\frac{z}{2\sqrt{Dt}}\right) \quad (5.6)$$

where H is microhardness, and $H_o \propto C_o$ and $H_s \propto C_s$.

Shamblen and Redden [32] reported Q_d as 202 kJ/mol according to microhardness method, for diffusion of oxygen in Ti-6Al-2Sn-4Zr-2Mo alloy in normal atmospheric condition between temperature range of 300-900°C. Frangini et al. [33] reported that, in air oxidation conditions between temperature range of 600 – 700°C, Q_d value of oxygen in Ti-6Al-4V alloy is in good agreement that of alpha titanium (200.6 kJ/mol). However, Q_d value has been reported between 130 – 286 kJ/mol for oxygen diffusion in alpha-titanium for different oxidation temperature as listed in Table 5.1 [36].

Table 5.1. Diffusion activation energy of oxygen in alpha titanium reported by various researchers [35,36].

Temperature (°C)	Activation Energy (kJ/mol)	Reference
460 – 700	200	[36]
593 - 760	240.8	[35]
650 – 875	197	[36]
700 – 850	196	[36]
700 – 950	200.6	[36]
750 – 850	130	[36]
750 – 1050	286	[36]
932 - 1142	203	[36]

Göbel et al. [28] investigated diffusion of oxygen to α phase pure titanium and $\alpha + \beta$ Ti-4Nb alloy by utilizing Equation. 5.6. after oxidation at 800°C for 5 and 150 hours in different atmospheres (Ar/O₂, Ar/O₂/H₂O, N₂/O₂, N₂/O₂/H₂) Ar/O₂/H₂O). After 150 hours exposure, the diffusion coefficients varied in between $0,9 \times 10^{-10}$ and $1,5 \times 10^{-10}$. Concerning the specimens exposed for 5 hours, slightly higher values were determined, i.e. $1,6 \times 10^{-10}$ and $3,6 \times 10^{-10}$. Microhardness measurements conducted on oxidized $\alpha + \beta$ Ti - 4Nb alloy revealed that, the diffusion coefficient of oxygen in the β phase is more than two orders of magnitude higher than the one in the α phase.

5.4. Stress Generation During Oxidation

The generation of stresses in the oxide scales and underlying diffusion zone, is an important issue during oxidation at high temperatures. Generally, the stresses acting on the oxide scales are compressive and arise from the thermal expansion coefficient mismatch between oxide scale and the substrate [37]. However, more elaborate mechanisms have been proposed about cracking of oxide scales at elevated temperatures [27,38-40]:

- Oxygen dissolution in metals: Large stresses may develop as a result of lattice expansion caused by the dissolution of interstitial oxygen atoms.
- Pilling-Bedworth ratio: This is simply the molar volume ratio of the formed oxide to consumed metal. In the case of inward growing oxide, if this ratio is higher than 1, formed oxide is constrained to occupy the volume of consumed metal. This situation constitutes the development of compressive stresses.

- Oxide growth mechanisms: Due to outward migration of metal ions through the oxide scale, voids and cavities are formed at or near the metal-oxide interface. Continued oxidation causes a build up of stresses in the oxide-metal system. Counter-current diffusion of metal ion and oxygen leads to the formation new oxide within the scale. As a result, oxide scale grows in thickness and laterally along the surface and this produces large stresses.
- Metal orientation: In polycrystalline materials stresses may develop at grain boundaries owing to the difference in oxidation rates between neighboring grains and a preferential diffusion and oxide formation along grain boundaries.
- Changes in oxide modifications: The transition of one oxide to into another results in a change of the scale density and generates stresses in the oxidized layers.

Unless the stresses are relieved, cracking of oxide scale or detachment of oxide scale from the substrate may occur. Cracking and rupture of oxide scales due to these stresses leads to increment of oxidation rate because of loss of protectivity of the oxide scale [27,38]. When oxide scales are thin, they may deform easily and remain adherent to substrate. As the thickness of the oxide scale increases, they exhibit resistance to deformation. If the oxide-metal interface has a high adhesive strength relative to the cohesive strength of oxide, cracking of the oxide is observed. Poor interfacial adhesion leads to decohesion of scale before cracking [27,37].

During parabolic oxidation of titanium alloys diffusion of oxygen through oxide scale and metal provides inward growth oxide and solid solution formation. Cracking and spallation of oxide scale is observed due to growth stresses. Also oxygen dissolution leads to large stresses and strain in the metal. Oxygen concentration reaching a value corresponds to $\text{TiO}_{0.35}$ causes structural changes in solid solution which is attributed to ordering of oxygen atoms in the titanium lattice. The expansion of lattice results in large compressive stresses and causes detachment of a layer of $\text{TiO}_{0.35}$. After the loss of protective nature of oxide scale, the rate of oxidation changes from parabolic to linear and heavy oxide formation begins to take place [27,29,37,38].

6. BIOMEDICAL APPLICATIONS OF TITANIUM ALLOYS

Titanium and titanium alloys are regarded as the materials of choice for long-term implantable devices. Surface properties are the main reason for the use of titanium in medical technology. Mechanical properties such as elasticity and specific strength (strength/weight ratio) are the additional advantage of titanium alloys over other metals including stainless steel and Co-Cr alloys. The combination of corrosion resistance, biocompatibility and mechanical performance makes them the most favorable material. Titanium alloys owe their corrosion resistance to surface oxide layer. This situation provides biocompatibility, which is defined as the ability of a material to perform an appropriate host tissue response in a specific application. Long-term experiences show that host tissue adapts to materials that fulfill its mechanical function. Low elastic modulus of titanium alloys relative to other metallic biomaterials puts them in the first place, especially for joint replacements [3,6].

Designing criteria for medical devices primarily relies on chemical and mechanical aspects of the material. Further evaluation distinguishes the available properties according to its priority for certain application. The earliest applications of titanium for surgical and dental devices started with the use of commercial purity titanium and Ti-6Al-4V alloy. Commercially pure titanium is used to produce dental implants, osteosynthesis plates and screws in joint replacements and also used in vascular and audiological applications. Due to their mechanical properties titanium alloys are used for production of higher load devices like intermedullary nails, locking bolts, fixation screws, interbody fusion cages and components of joint-replacement systems. Some examples of titanium alloy medical devices are displayed in Figure 6.1.

Clinical studies and retrieval examinations showed the evidences of excessive wear at the bearing surfaces in titanium based implants. Since creation and accumulation of wear debris produce an adverse tissue response, wear induced particle release from implant surfaces and simultaneous corrosive attack of biological environment

was always a matter of concern for titanium based medical devices due to their toxic effects. The release of damaging enzymes and bone cell lysis resulted in pain and implant loosening [4,6,41].

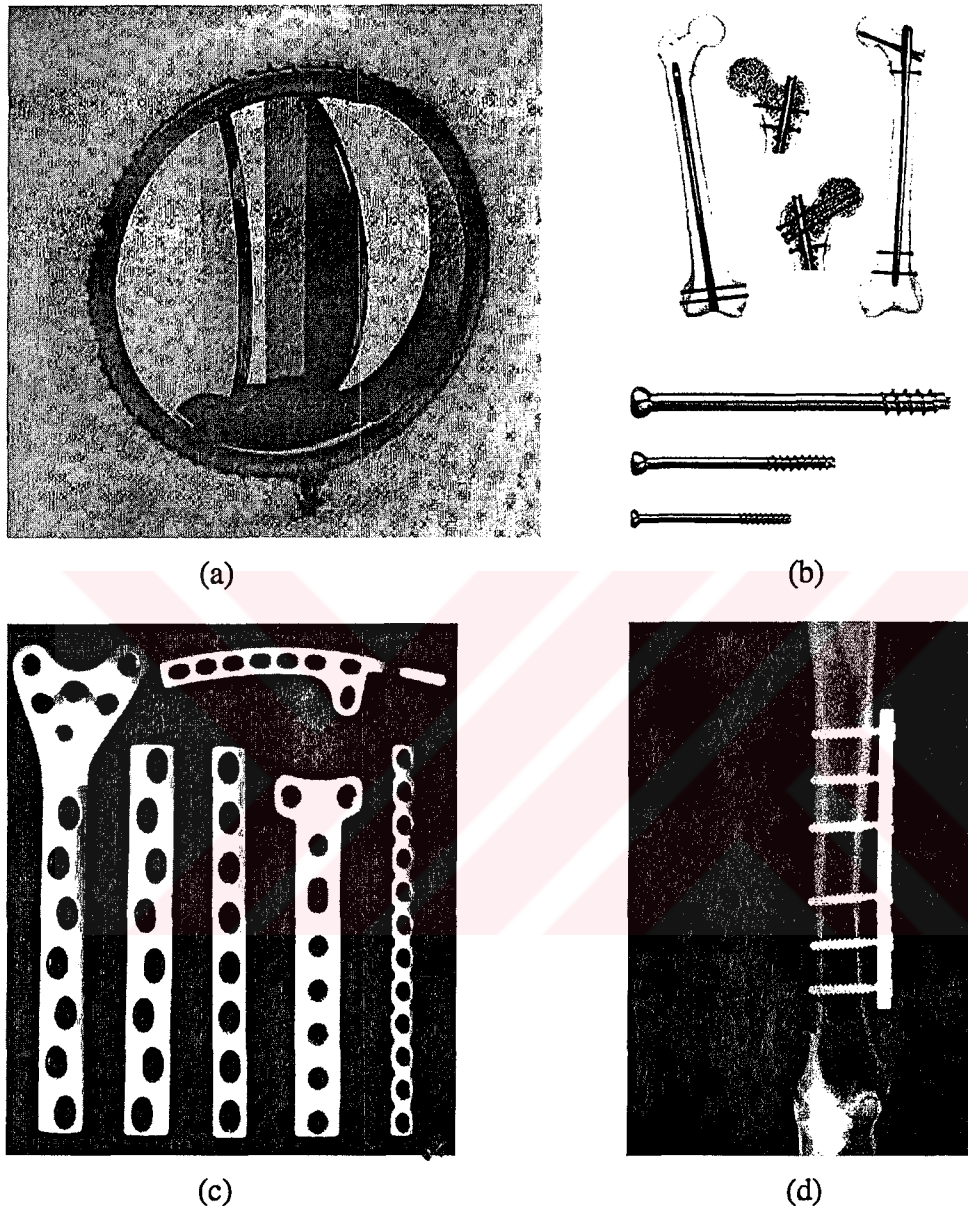


Figure 6.1. Some examples of titanium alloy medical devices; (a) heart valve, (b) bone fixation nails, (c) bone plates and (d) bone plate with fixation screws [3].

The design features and parts making up the medical devices should be described, in order to understand the corrosion and wear mechanism. In hip joint replacements, the articulating bearings are femoral head and acetabular cup. They are positioned in such a way that they reproduce the natural movement inside the hip joint. The hip stem is fitted permanently in the femur bone. In modular designs, femoral head is

connected to stem by conical taper necks. Femoral stem can be press fitted in bone or fixed with bone cement based on polymethylmetacrylate (PMMA). Generally, ultrahigh molecular weight polyethylene (UHMWPE) acetabular cups are used in conjunction with titanium alloy femoral heads. Knee prostheses generally consist of a femoral component and a tibial component, plus a patella made of UHMWPE. Hip and knee replacement systems can be seen in Figure 6.2. Bone screws are mostly used for bone fixation by exerting compression on the fracture gap or for the fixation plates and other devices to the bone. Bone plates are applied for the treatment of long- bone fractures [3].

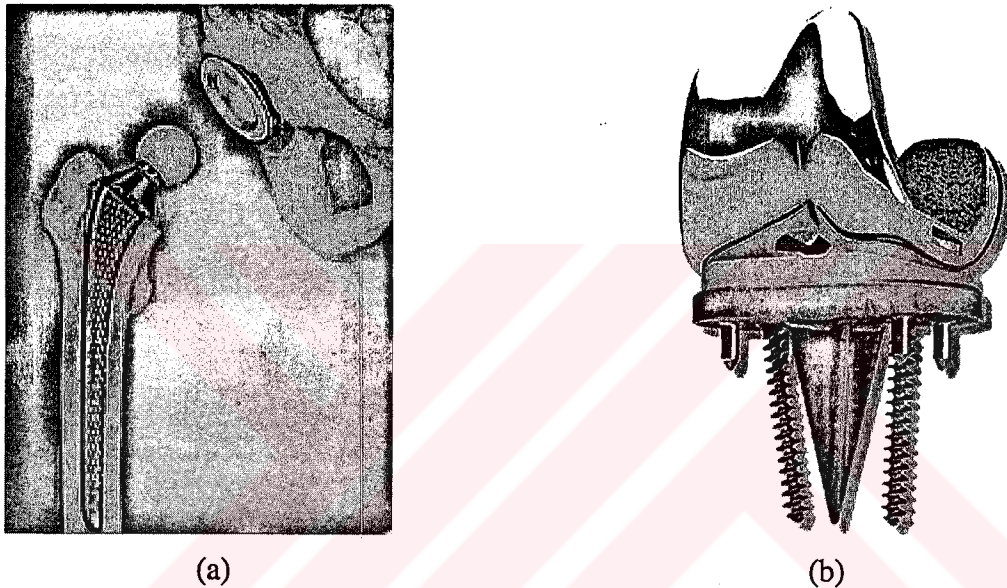


Figure 6.2. (a) Hip and (b) knee joint replacement systems [42,43].

In the light of above considerations, titanium medical devices are inevitably subjected to fretting and sliding wear and consequently wear assisted corrosion. The factors affecting the type and amount of wear that occurs in medical devices can be defined by four main wear modes shown in Figure 6.3.

Mode 1 refers to articulation between to primary bearing surfaces. This mode is observed between the femoral head and the interior of acetabular cup in hip prostheses or between the femoral condyles and the tibial plateau of knee prostheses.

Mode 2 occurs whenever a primary surface articulates directly against a non-bearing surface. This is observed when the UHMWPE component is worn out. Contact

occurs between the primary bearing surface and the secondary surfaces like the metal backing or the supporting bone.

Mode 3 occurs whenever two primary bearing surfaces are still articulating together but third-body particles become entrapped between them. Such contamination can include fragments of PMMA cement, bone chips and metallic fragments.

Mode 4 occurs whenever two secondary non-bearing surfaces rub together. In a hip prosthesis, for example, this can include fretting between metal screw and the acetabular shell or liner, neck-socket impingement, fretting of the conical connection between the head and the stem, pistoning between the stem and cement mantle or surrounding bone. Fretting also occurs on the screw and plate connections between themselves and bone. The wear particles generated by Mode 4 (metallic, PMMA or bone) can migrate to articulating primary surfaces, thereby inducing Mode 3 wear [3,44].

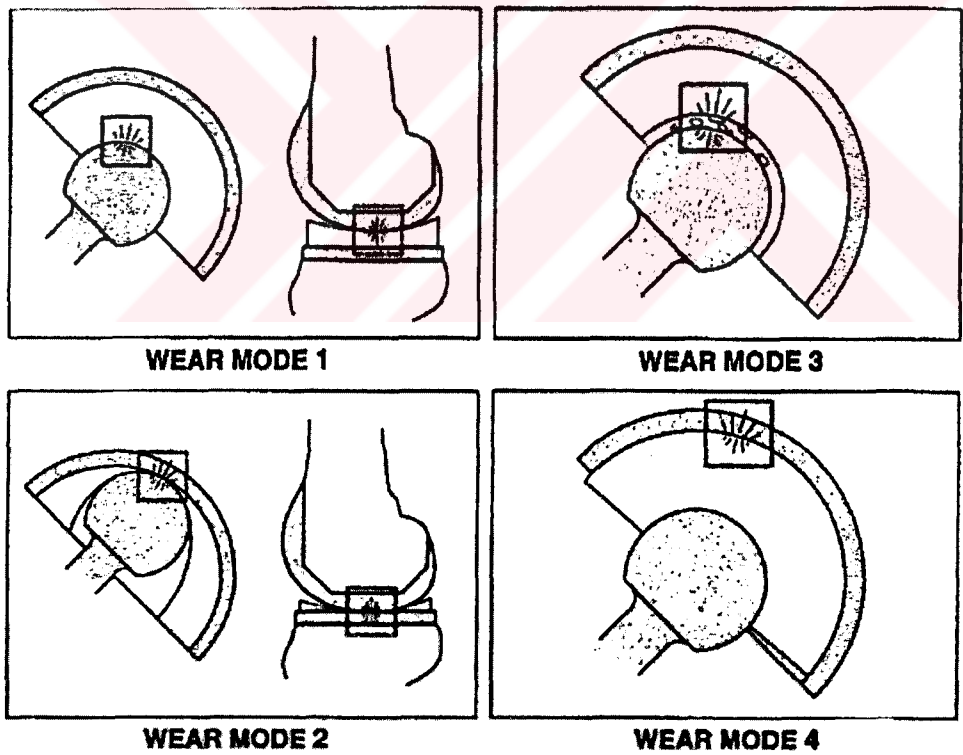


Figure 6.3. Wear modes that are observed on orthopedic implants [44].

7. EXPERIMENTAL

This research aimed to investigate the corrosion and wear performance of a thermally oxidized Ti-6Al-4V alloy. Experimental procedure was composed of three main sections;

- Oxidation treatments,
- Characterization tests and
- Performance tests.

7.1. Oxidation Treatments

In this study, the well-known titanium alloy Ti-6Al-4V was subjected to investigation of thermal oxidation treatments. It was received as 8 mm diameter cold drawn rod. Oxidation treatments were conducted at various temperatures ranging between 500-850 °C, for different time intervals between 1-72 hours at normal atmospheric condition. Cylindrical specimens that were cut from the rod, successively ground on 240-1200 mesh SiC abrasive papers. Final polishing was conducted with fine grade Al₂O₃ slurry abrasive to achieve mirror like surface finish. Later they were cleaned in acetone and dried in hot air. Isothermal oxidation was carried out in Nabertherm laboratory type furnace. Weight measurements of the specimens were made to 0,1 mg accuracy, before and after the oxidation treatments. For each oxidation condition three samples were utilized and the weight gain values were averaged according to the results of these three samples for further analysis.

7.2. Characterization Tests

Characterization of the untreated and oxidized samples was carried out by, microscopic examinations, surface roughness measurements, x-ray diffraction analysis and hardness measurements.

7.2.1. Microscopic Examinations

Zeiss light optical microscope utilized to reveal the surface features of oxidized samples. Further microstructural examinations were conducted on cross-sections prepared by standard metallographic technique. In order to elucidate the microstructural evolution, several types of etching reagents were used, including Kroll's reagent and 2 % HF solution.

7.2.2. Surface Roughness Measurements

Mahr Perthen Perthometer S8P optical profilometer was used to examine the surface roughness of untreated and oxidized samples. The effect of oxidation conditions on surface roughness was determined according to average roughness values.

7.2.3. X-ray Diffraction Analysis

Philips RV 3710 X-ray diffractometer was used for the examinations. The glancing incidence X-ray diffraction technique (GXRD) was used for surface phase identification of oxidized samples, using a Cu K_{α} radiation source. Diffraction angle scan range was between 10-90°, with a step-increment angle of 0,02° and a count time of 1 s.

7.2.4. Hardness Measurements

Hardness measurements were carried out by utilizing Fisher HP 100 XY-PROG ultramicrohardness tester and Tukon Model LL microhardness tester with the vickers indenter.

During ultramicrohardness measurements indentation load-depth data were recorded. The indentation procedure consisted of 60 steps, and the waiting period between

steps was 1 s. Hardness measurements were performed under varying loads ranging between 100-1000 mN on the surface of the untreated and oxidized samples. Additionally, hardness measurements have been carried out on the metallographic polished cross sections of the oxidized samples with indentation load of 50 mN.

In order to evaluate the effects of oxidation temperature and time on the core hardness of the samples, microhardness tests were made under a load of 1 kg. Microhardness values of untreated and treated samples analyzed in conjunction with microstructural changes.

7.3. Performance tests

Performance of the untreated and oxidized samples was determined by corrosion and wear tests.

7.3.1. Corrosion Tests

Immersion-corrosion tests were conducted to evaluate the relative corrosion resistance of untreated and oxidized samples. Cylindrical specimens were hole drilled through longitudinal direction and polished before oxidation treatments. Untreated and oxidized samples were suspended in corrosive solution for 60 hours. A reducing acid environment composed of 5 M HCl solution was used for accelerated corrosion testing. The minimum amount of the solution was determined by taking into account the surface area of the samples as 0,3 ml/mm² [45]. During the corrosion tests the temperature of the solution was 24±4 °C. Weight measurements with an accuracy of 0,1 mg were made before immersion and during run in period of immersion. Weight loss data and visual examinations were reported. After the testing time the corroded surfaces of the samples were examined by a microscope with 10X magnification.

7.3.2. Wear Tests

Wear tests were conducted on a reciprocating wear tester, under a normal load of 150 g with a 10 mm diameter Al₂O₃ ball. Wear tests were made in normal atmospheric conditions with 40 % humidity (dry sliding wear) and in commercially available

ISOTONIC serum containing 0.9 % NaCl (corrosion wear). A sketch of reciprocating-sliding wear tester is displayed in Figure 6.1. Sliding speed of the ball on the samples was 1,6 mm/s. Wear tests were interrupted in certain intervals to determine the progress of wear. At each interval samples were cleaned with alcohol and wear tracks were examined by surface profilometer and an optical microscope. After examining the wear tracks developed on the surfaces of the specimens they were put back to the wear tester in the original arrangement. Wear tests were performed up to 300 minutes.

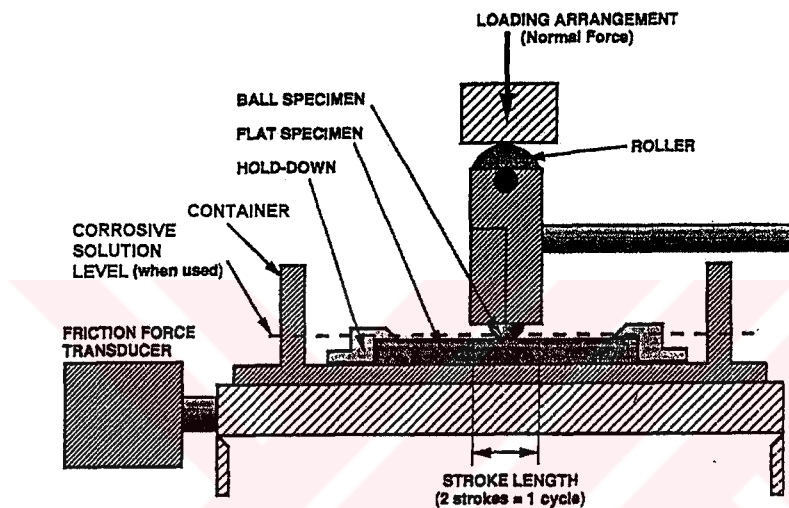


Figure 7.1. Schematic view of the reciprocating wear tester.

8. RESULTS AND DISCUSSION

8.1. Characterization of the Investigated Material

Optical micrographs displaying the longitudinal and transverse cross-sections of the as-received Ti-6Al-4V alloy are given in Figure 8.1. The alloy has typical $\alpha + \beta$ structure with elongated grains in longitudinal direction. The microhardness of the examined alloy was measured as 345 HV under the indentation load of 1 kg.

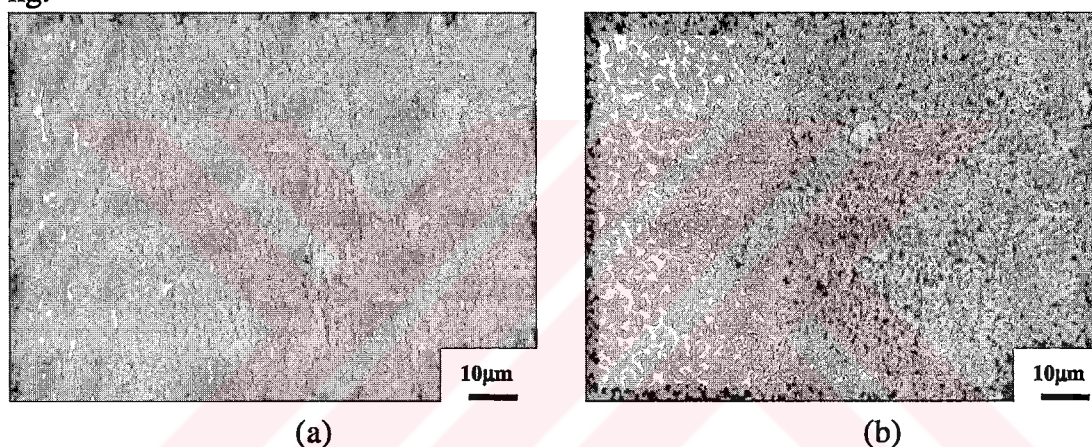


Figure 8.1. (a) Longitudinal and (b) cross-sectional micrographs of the investigated Ti-6Al-4V alloy in as-received condition.

8.2. Determination of Optimum Oxidation Conditions

Optical micrographs of the longitudinal sections of oxidized samples are given in Figure 8.2. Beneath the oxide layer oxygen diffusion zone appeared in white color after etching. At low temperature, relatively thin oxide films were observed which remained integral with the subsurface oxygen diffusion zone (Figure 8.2 a). Increasing temperature and exposure time promoted, formation of thick oxide layers and deeper penetration of oxygen into the metal (Figure 8.2 b). The variation of oxide layer thickness and oxygen diffusion zone with respect to oxidation conditions are presented in Figure 8.2. Since oxide scales were detached from the substrate for high oxidation temperatures (Figure 8.2 c, d, e,

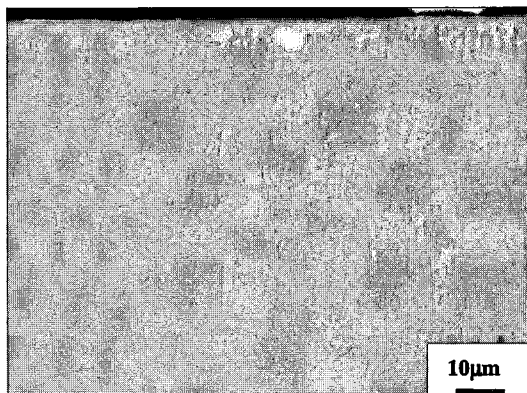
Imbrie et al. [38] investigated the evolution of oxide scale during oxidation of commercially pure titanium at 700°C. They reported that after 10 hours of exposure, oxide scale was coherent with the substrate and free of any defects. As the exposure time increased, formation of numerous voids was observed. After prolonged exposure time, layered structure of oxide scale was evidenced. Porous layers were growing parallel to the oxide-metal interface and cracks developed between the porous layers. Cracks either continued growing in a direction parallel to the oxide-metal interface or changed direction and propagated to the surface.

Coddet et al. [46] studied the oxidation of commercially pure titanium in temperature range of 500-700°C and claimed that the adhesion strengths of oxide layers were relatively high for temperatures below 650°C while they tended to zero at 700°C.

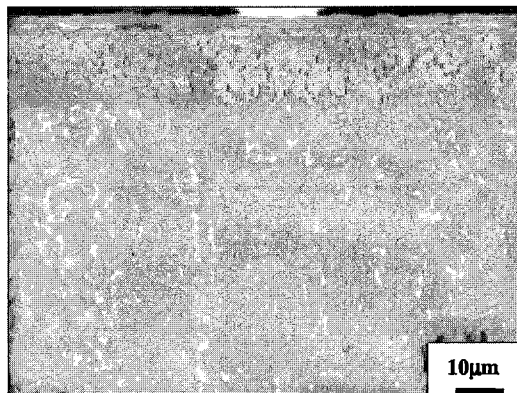
Frangini et al. [33] reported that oxidation of Ti-6Al-4V alloy at 600°C gave a gray, dense and adherent oxide film and there was no evidence of cracking even at the longest exposure time. However, at 650°C the onset of an oxide scale with a layered structure was noted. They claimed that, layered nature of the scale was gradual and dependent on time. They also observed uniformly distributed voids throughout the scale and the developing fissures between oxide grains.

Du et al. [34] proposed that the stresses caused by thermal expansion mismatch between the oxide scale and substrate was released by cracking initially at the edges of the specimen and expanded progressively through the entire specimen surface.

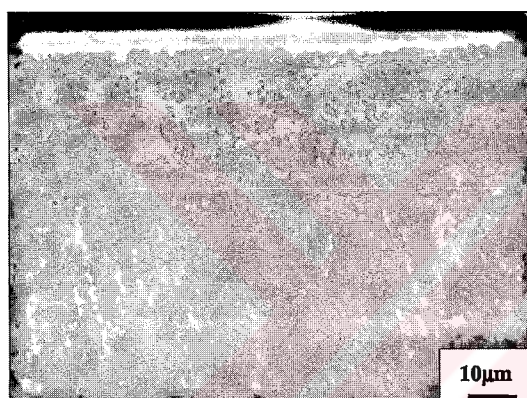
Garbacz and Lewandowska [40] studied the oxidation of several titanium alloys at 900°C. They found that the oxide scale formed on Ti-6Al-4V alloy showed numerous cracks and delamination.



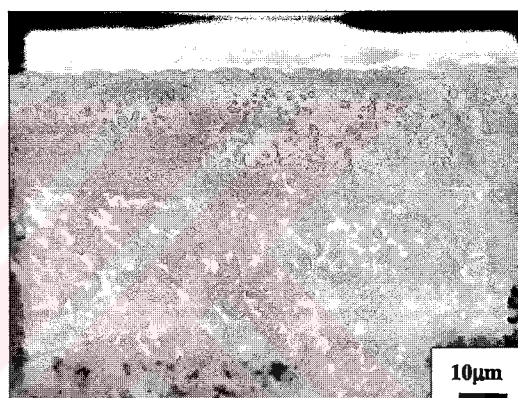
(a)



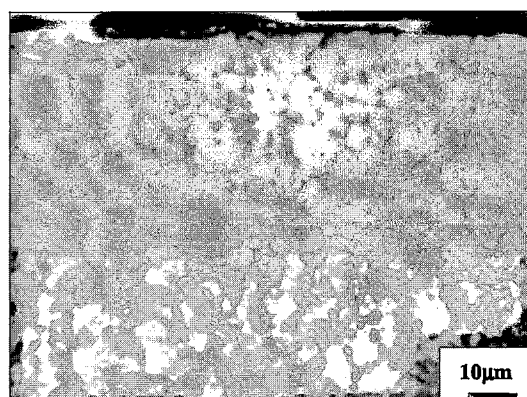
(b)



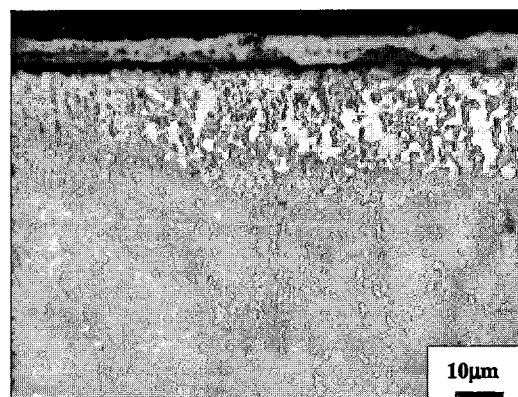
(c)



(d)



(e)



(f)

Figure 8.2. Cross-sectional optical micrographs of the oxidized samples;(a) 600°C-72 h, (b) 650°C-72 h, (c) 700°C-48 h, (d) 750°C-12 h, (e) 800°C-12 h, (f) 850 °C-1 h.

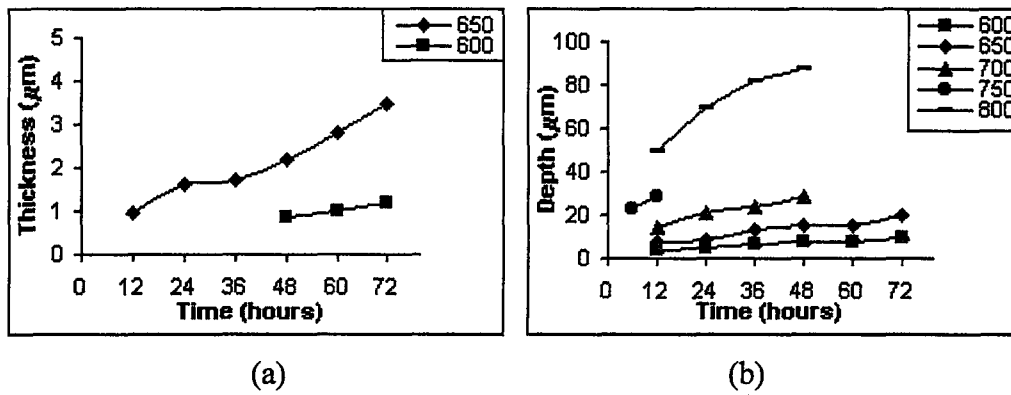


Figure 8.3. The effect of oxidation time and temperature on the (a) thickness of oxide layer and (b) depth of oxygen diffusion zone.

Bulk microstructures of oxidized samples are presented in Figure 8.4. Recrystallization of cold deformed metal occurred after extended exposure time at lower temperatures. At high temperatures, recrystallization followed by grain growth and resulted in large equiaxed α grains. Also large β grains were observed at α grain boundaries.

Bulk hardness of the oxidized samples is given in Figure 8.5 with respect to oxidation temperature and time. Bulk hardness decreased upon oxidation, especially above 650°C in accordance with Figure 8.4 d, e, f. Figure 8.5 also reveals that, oxidation at 500°C cause increment in bulk hardness due to precipitation of Ti_3Al intermetallics [47,48]. Since oxidation at 500°C did not offered a measurable thickness of oxide layer and oxygen diffusion zone with an optical microscope, this temperature is excluded in the present study for oxidation treatments. Therefore optimum oxidation temperatures were determined as 600 and 650 C for the examined cold deformed Ti-6Al-4V alloy.

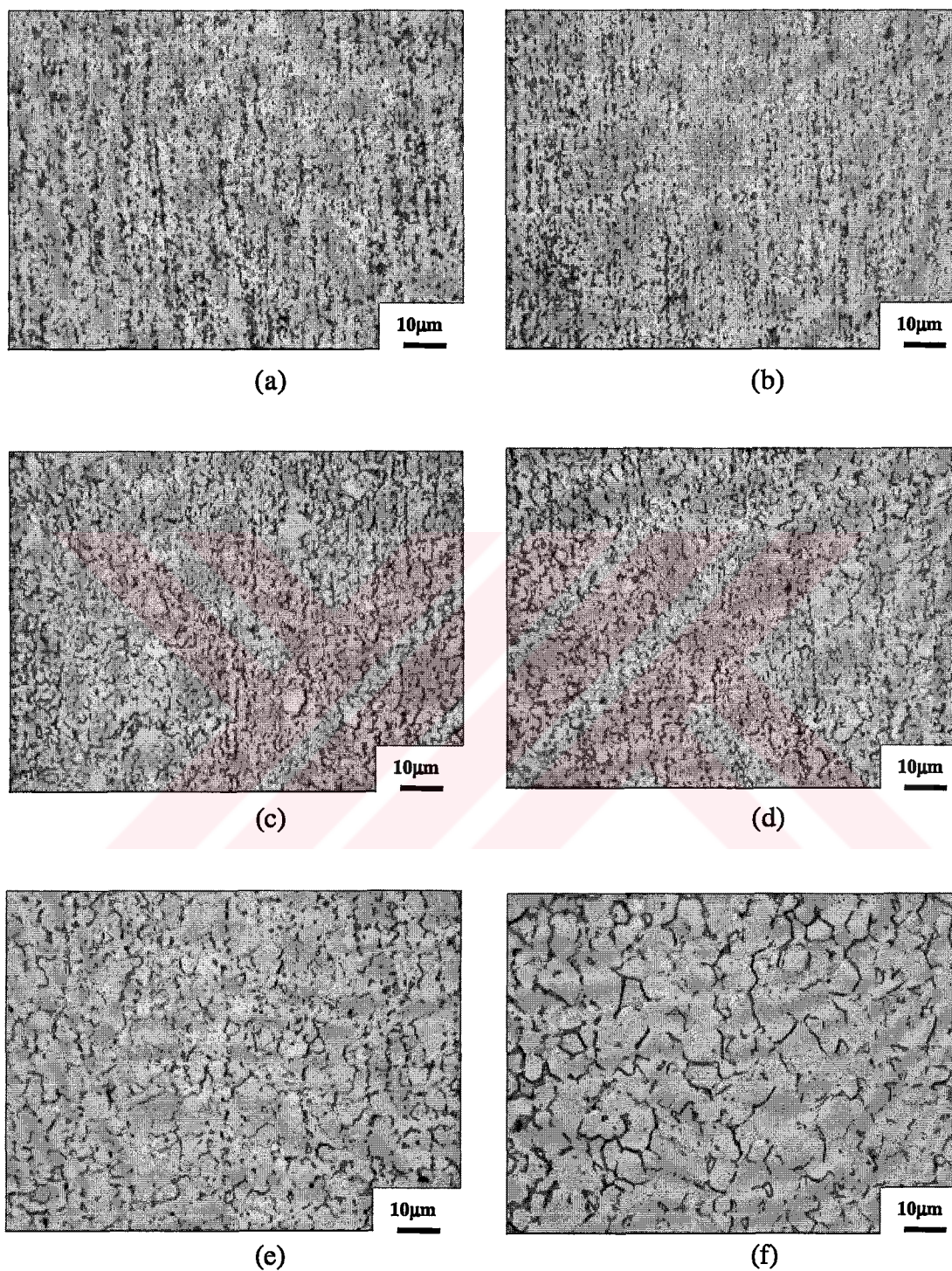


Figure 8.4. Bulk microstructures of the oxidized samples; (a) 500°C–48 h, (b) 600°C–48 h, (c) 650°C–48 h, (d) 700°C–12 h, (e) 750°C–12 h, (f) 800°C–48 h.

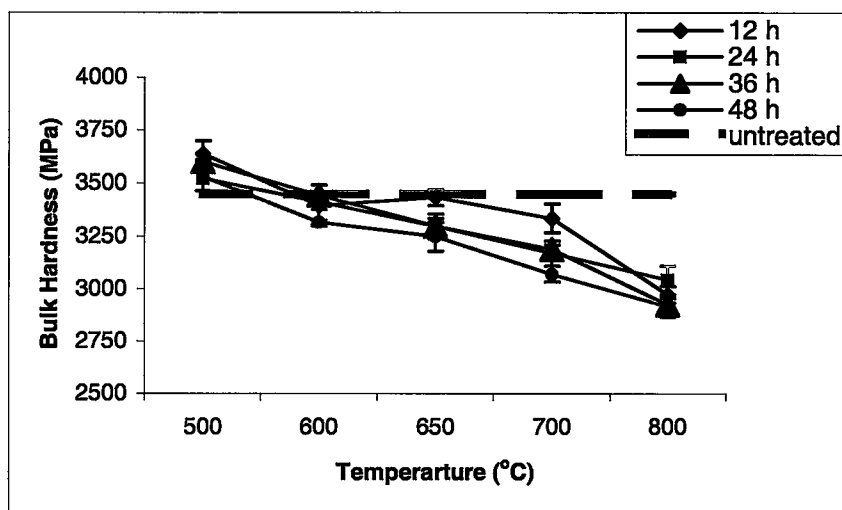


Figure 8.5. The effect of oxidation temperature and time on the bulk hardness of the examined Ti-6Al-4V alloy.

8.3. Characterization of Oxidized Surfaces

Microstructural characteristics of the surfaces oxidized at 600 and 650 C are presented by optical micrographs and XRD patterns in Figures 8.6 and 8.7 respectively (also see Figures A.1, A.2 in Appendix). Oxide layers are made of numerous small grains (Figure 8.6) and composed of anatase and rutile structures of TiO_2 (Figure 8.7). Increasing temperature enhanced the formation of rutile structure where anatase peak intensity abruptly decreased. X-ray diffraction patterns also show that, peaks of untreated alloy were slightly shifted after oxidation, which indicates solid solution formation beneath the oxide layer due to diffusion of oxygen.

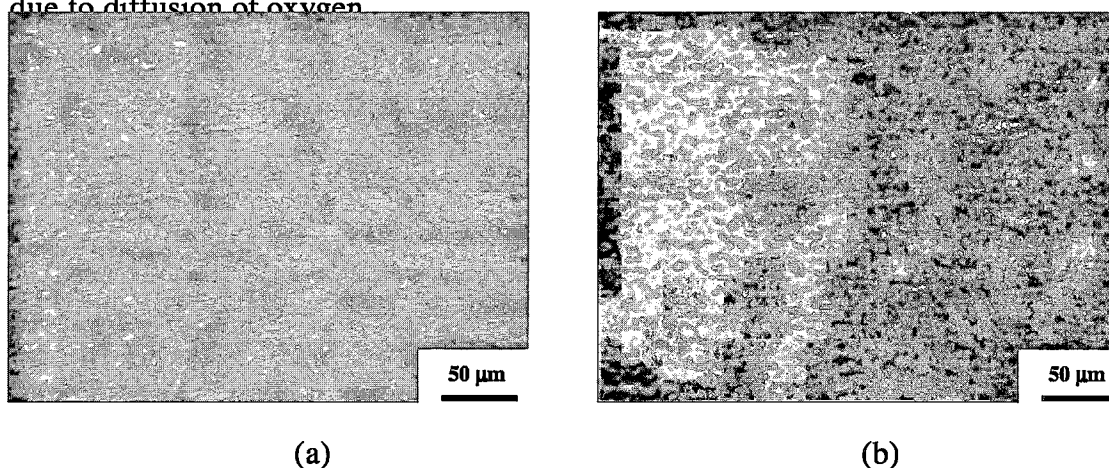
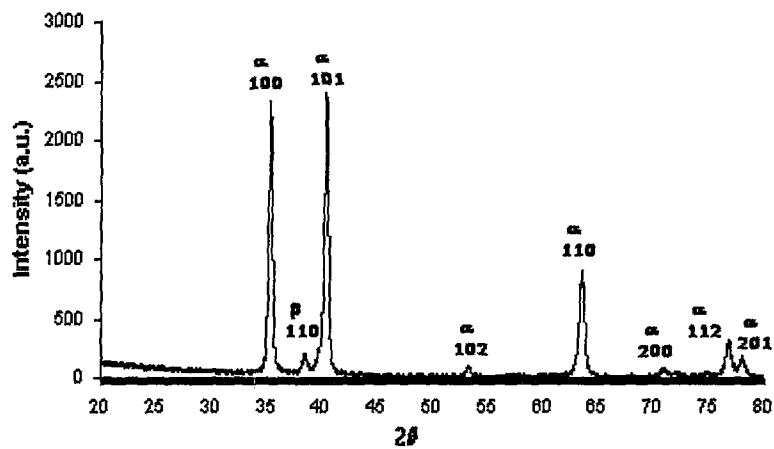
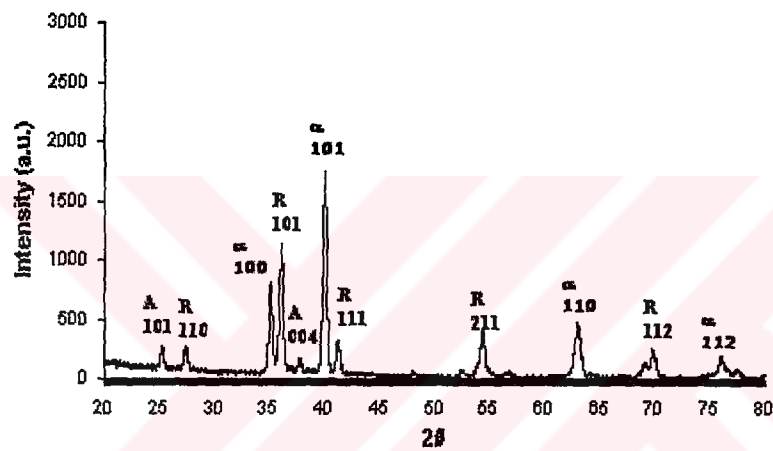


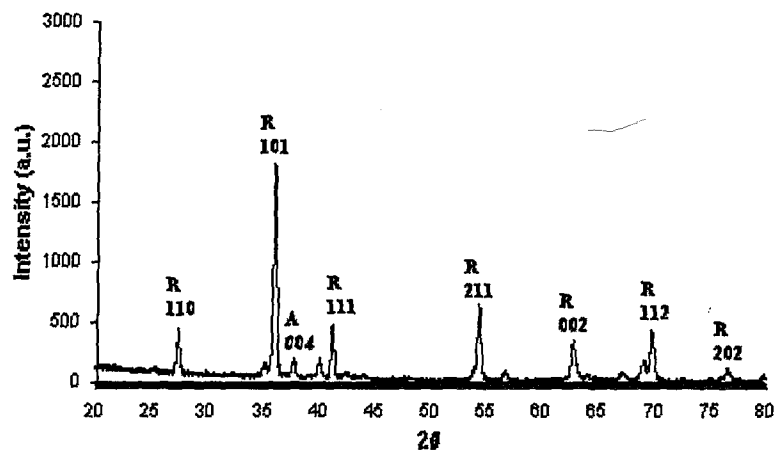
Figure 8.6. Optical micrographs of oxidized surfaces; (a) 600°C–60 h and (b) 650°C–12 h.



(a)



(b)



(c)

Figure 8.7. XRD patterns of untreated and oxidized surfaces; (a) untreated, (b) 600°C-72 h, (c) 650°C-72 h (α: hcp titanium, β: bcc titanium, A: anatase, R: rutile)

Average roughness (Ra) values of oxidized surfaces are depicted in Figure 8.8. Oxidation caused a drastic increase in roughness, where the average roughness of untreated sample was 0,17 μm before oxidation. Roughness of oxidized surfaces increased with increasing oxidation time and temperature.

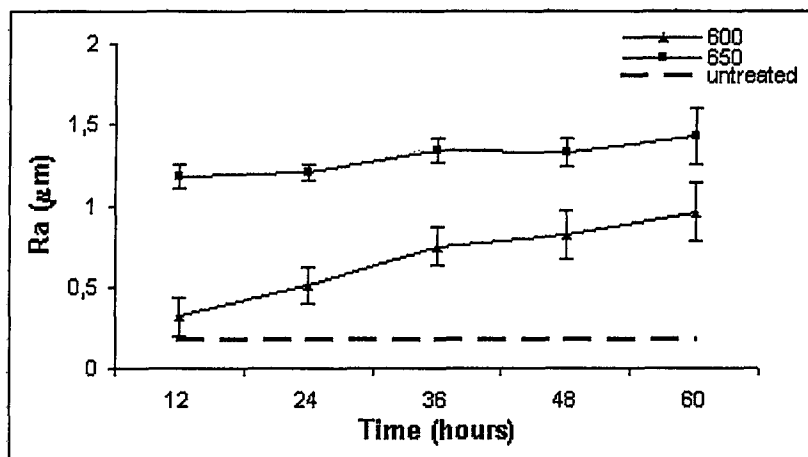
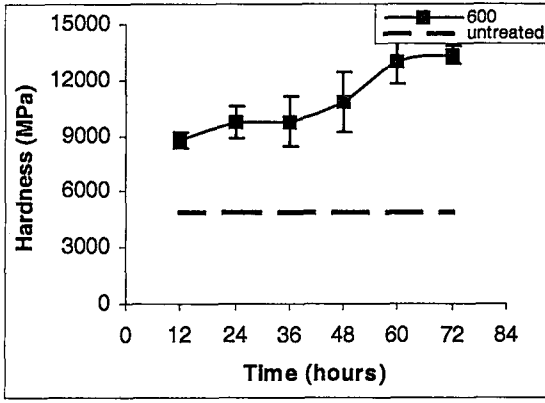


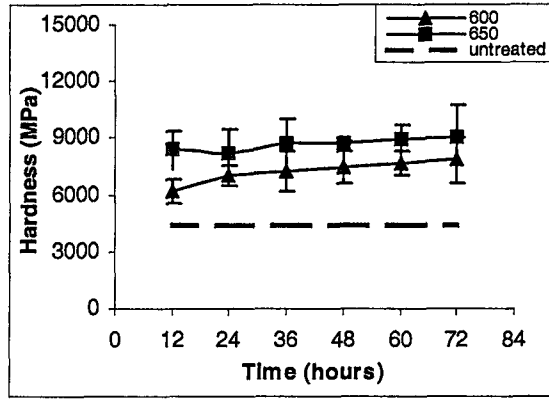
Figure 8.8. The effect of oxidation temperature and time on the average roughness of oxidized surfaces.

Surface hardness values of oxidized samples are given in Figure 8.9. It is clearly seen that higher oxidation temperature and time provided harder surfaces. It should be mentioned that, hardness measurements with an indentation load of 100 mN yielded higher hardness values than higher indentation loads. However, utilization of 100 mN was restricted for the specimens oxidized at 650°C due to its high surface roughness, which caused the severe scatter of hardness data [21,49].

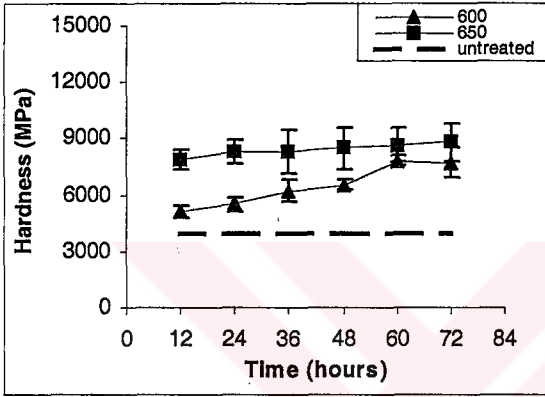
Surface hardness of untreated and oxidized samples under varying loads is presented in Figure 8.10. In untreated samples the hardness is almost constant for indentation loads in range between 250 and 1000 mN. However, dramatic increment in surface hardness was achieved upon oxidation. On the oxidized surfaces the decrease of hardness with increasing indentation load can be attributed to the involving of soft regions at high penetration depths of the indenter. It should be mentioned that, high hardness values were maintained for a wide indention load range, with increasing oxidation time and temperature. This indicates that, deeper hardened layers were achieved at high oxidation temperatures and/or exposure times.



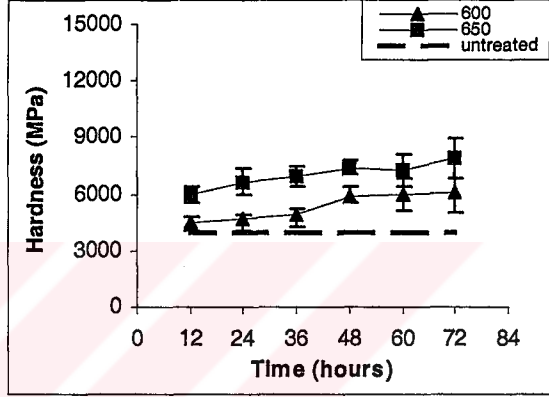
(a)



(b)



(c)



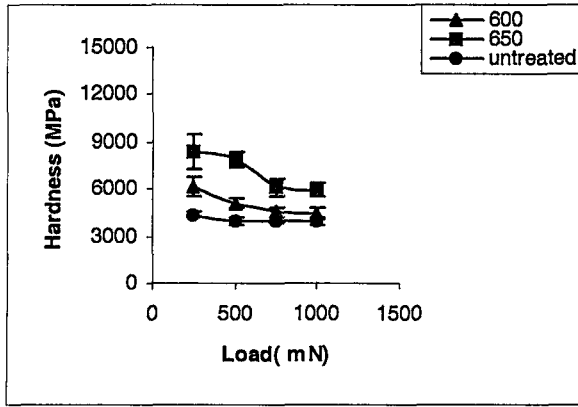
(d)

Figure 8.9 Surface hardness of oxidized samples measured under different indentation loads; (a) 100 mN, (b) 250 mN, (c) 500 mN, (d) 1000mN.

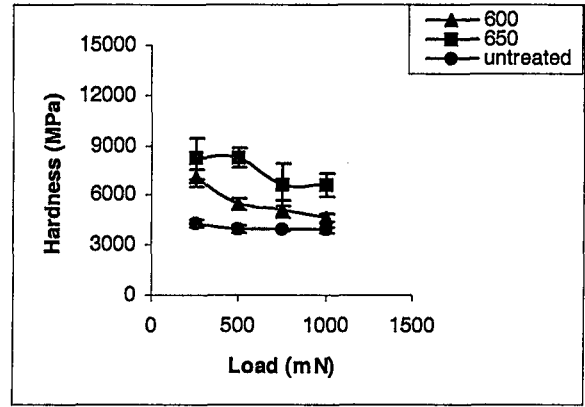
As mentioned in Chapter 5.4, residual stresses appear on the oxidized surfaces. In the present study, residual stresses were determined by instrumented indentation method under the indentation loads of 100 and 250 mN. This method involves the analysis of “indentation load-depth” data, according to the method of Suresh and Giannakopoulos [50]. Recently, Atar et al. [51] proposed a more realistic approach to indentation method by the aid of well-established XRD technique and reported following equation;

$$\frac{A}{A_o} = \left\{ 1 + \left(\frac{\sigma_r}{P_{ave}} \right) \right\}^{-1} \quad (8.1)$$

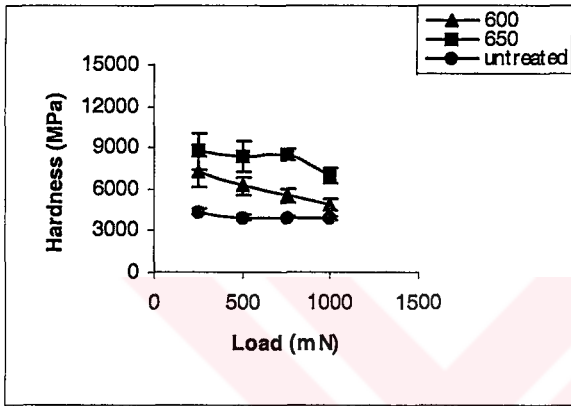
where A and A_o are the indentation contact areas with and without residual stress (σ_r), respectively. P_{ave} is the average contact pressure or equivalently the hardness.



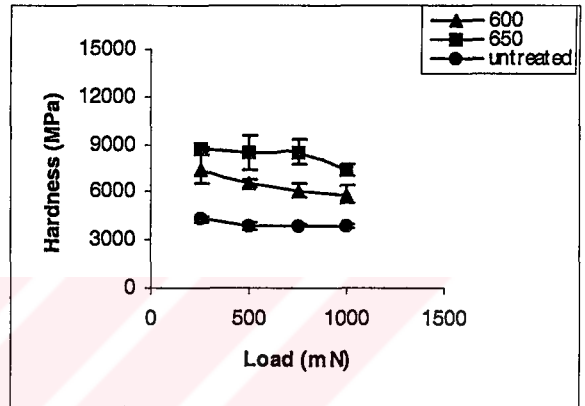
(a)



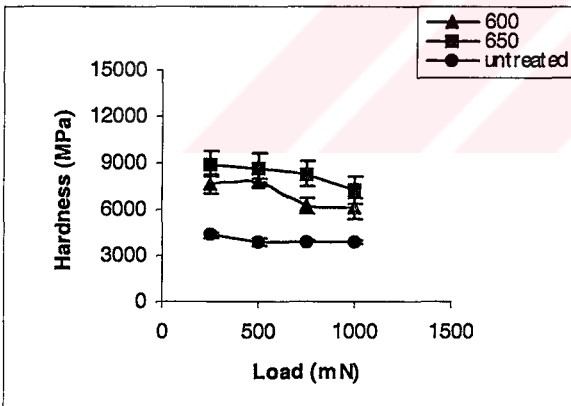
(b)



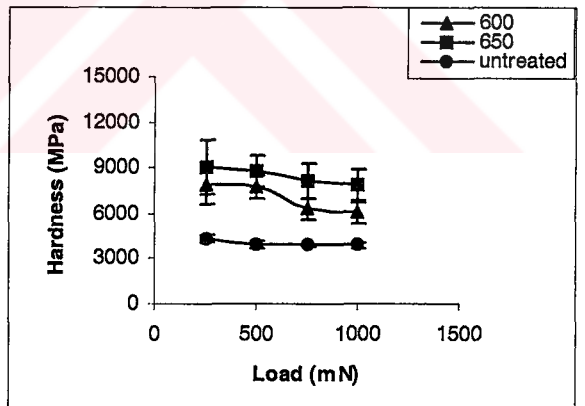
(c)



(d)



(e)



(f)

Figure 8.10. The effect of oxidation temperature and time on the hardness of oxidized surfaces; (a) 12 hours, (b) 24 hours, (c) 36 hours, (d) 48 hours, (e) 60 hours, (f) 72 hours.

Figure 8.11 presents the variation of residual stress during oxidation at 600 and 650°C. At 600°C residual stress increased from 3.5 GPa to 6 GPa with increasing oxidation time. This observation is more evident if the indentation load of 100 mN is used in Eq.1. 250 mN did not provide sufficient sensitivity for correlation between

oxidation time and residual stress for both 600 and 650°C of oxidation, due to higher penetration depths of indentation than oxide thickness and/or oxygen diffusion hardened zone.

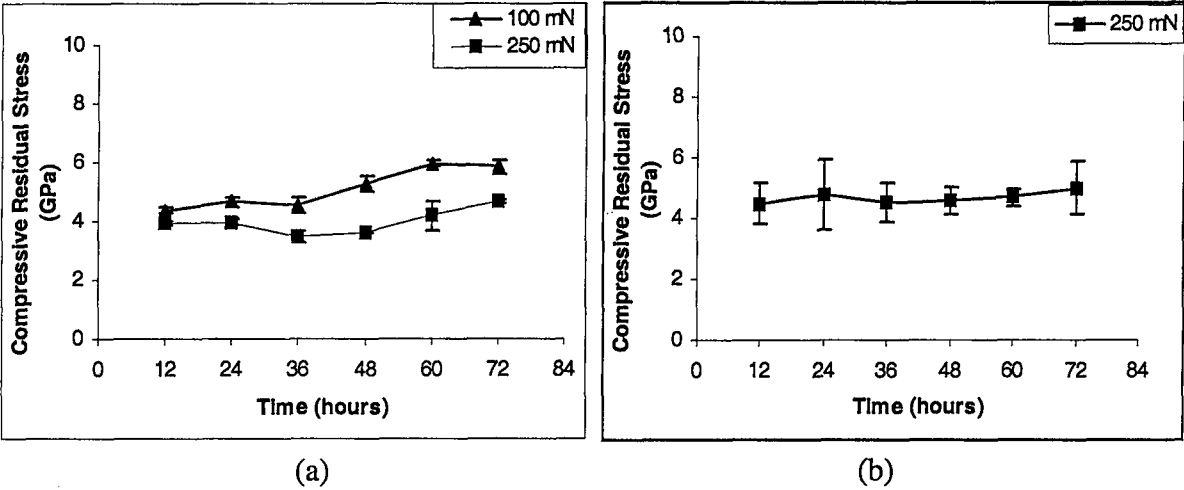


Figure 8.11. Residual stresses of the surfaces oxidized at (a) 600°C and (b) 650°C.

8.4. Kinetics of Oxidation and Diffusion

8.4.1. Oxidation Kinetics

Figure 8.15 shows the weight gain data of the samples during oxidation at 600 and 650°C. Since a parabolic correlation is evident in Figure 8.12, according to the theory of oxidation discussed in Chapter 5.3. Figure 8.12 is re-plotted by taking the square of weight gain data. Linear relationship exists for both oxidation temperatures as seen in Figure 8.13. Therefore, oxidation rate constant k is calculated as $1,5 \times 10^{-3}$ for 600°C and $1,02 \times 10^{-2}$ for 650°C from the slopes of Figure 8.13.

Since the oxidation rates of two different temperatures are known, activation energy for oxidation can be obtained as 257 kJ/mol by utilizing the Arrhenius equation (Equation 5.3), which is in good accordance with the previous results as mention in Chapter 5.3

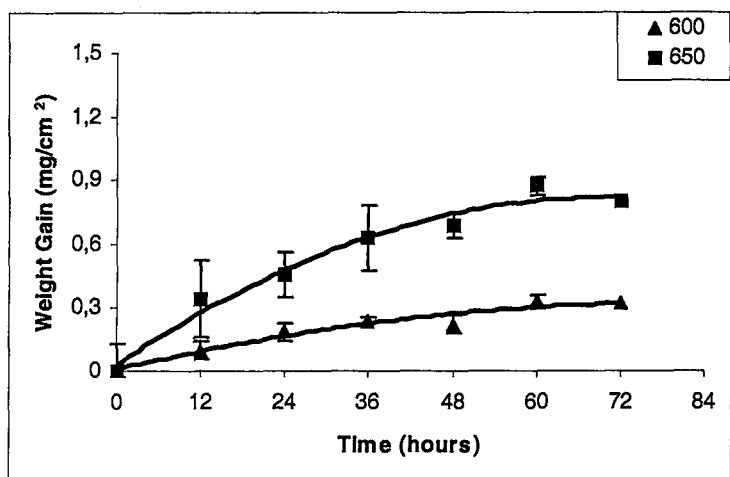


Figure 8.12. Weight gain of Ti-6Al-4V alloy during oxidation at 600 and 650°C.

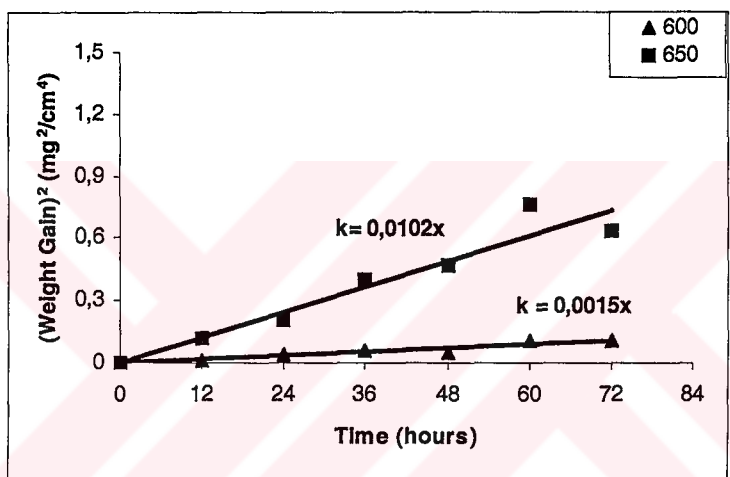
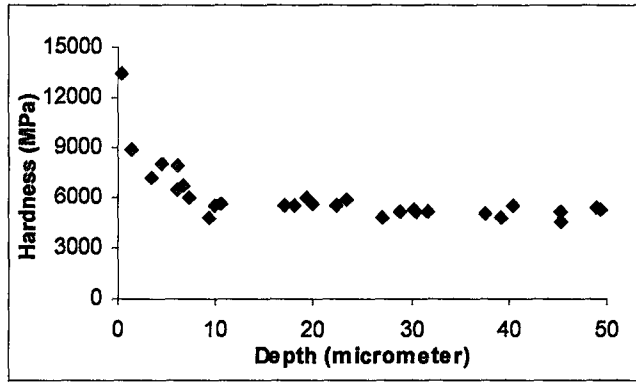


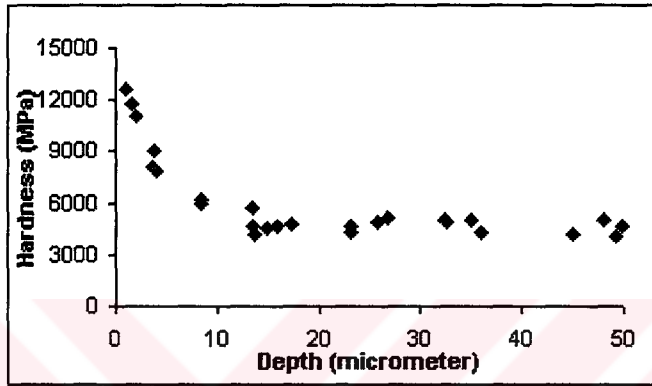
Figure 8.13. Re-plotting of Figure 8.12 providing the oxidation rates at 600 and 650°C.

8.4.2 Oxygen Diffusion Kinetics

The case depths of the oxidized samples are given in Figures A.3, A.4, A.5, A.6 in appendix. Gradual decrease of hardness from surface to the core was evident in hardness – depth plots. Obviously, oxidation at higher temperature for longer times promoted harder surfaces that were extended to larger depths of base metal. In Figures 8.14 and 8.15 hardness profiles of the samples that are oxidized at temperatures 600 and 650°C for exposure times of 60 and 72 hours are presented, respectively.



(a)



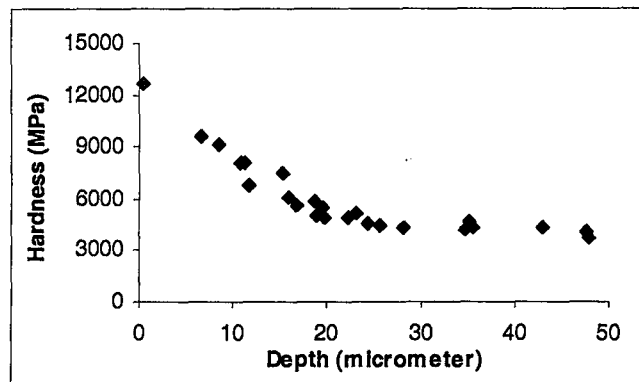
(b)

Figure 8.14. Hardness- depth profiles of oxygen diffusion zones after oxidation at 600°C (a) 60 hours, (b) 72 hours.

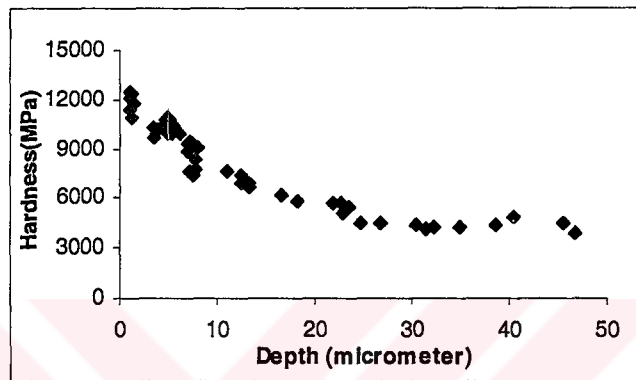
Hardness-depth profiles presented in Figures 8.14 and 8.15 obey the following equation

$$H = H_s e^{-az} \quad (8.2)$$

where H is the hardness at depth z , H_s is the surface hardness ($z = 0$) and a is the constant that gives the steepness of the profile. In Table 8.1 H_s and values of individual profiles are given



(a)



(b)

Figure 8.15 Hardness - depth profiles of oxygen diffusion zones after oxidation at 650°C (a) 60 hours, (b) 72 hours.

Table 8.1. The constants of Equation 8.2 calculated from Figures 8.14 and 8.15.

Temperature (°C)	Time (h)	H_s (Mpa)	a
600	60	11603	0,0863
	72	12750	0,0943
650	60	13035	0,0457
	72	12333	0,0441

According the data listed in Table 8.1, the solution of Equation 5.6. yields the value of oxygen diffusion coefficient for each oxidation temperature and time, as given in Table 8.2.

Table 8.2. Diffusion coefficient values calculated from Equation 5.6.

Temperature (°C)	Time (h)	Diffusion Coefficient (cm ² /s)
600	60	$8,8 \pm 0,4 \times 10^{-13}$
	72	$6,8 \pm 0,6 \times 10^{-13}$
650	60	$3,9 \pm 0,3 \times 10^{-12}$
	72	$3,1 \pm 0,3 \times 10^{-12}$

Since the diffusion coefficient values at two different temperatures are known for a certain exposure time, the activation energy for oxygen diffusion in Ti-6Al-4V alloy

can be calculated by utilizing the Arrhenius equation (Equation 5.5), as 199 kJ/mol and 200 kJ/mol for oxidation times of 60 h and 72 h, respectively. These values are in good accordance with the results of listed in Table 5.1.

8.4.3. Prediction of the Depth of Oxygen Diffusion Zone

In particular, the depth of oxygen diffusion zone (ODZ) extends with respect to temperature and time variables. For a given alloy, the plot of a single parameter that combines temperature and time, versus ODZ depth may establish the parametric relationship for the diffusion process. This kind of relationship, reducing the temperature and time variables into one parameter is suggested for estimating the creep behavior of materials by Sherby-Dorn, who introduced a temperature compensated time parameter θ , as [52];

$$\theta = t \exp\left(-\frac{Q}{RT}\right) \quad (8.3)$$

In Equation 8.3. t is time, T is temperature, R is gas constant and Q is activation energy for creep. θ also has units of time as Q/RT is dimensionless (Q : J/mol, R : J/mol/K, T : K). If the creep strain is a function of θ (at the same stress level), plotting creep strain versus θ allows to interpolate between different temperatures and times.

In analogy, Equation 8.3 can be utilized for predicting the diffusion depth of oxygen in Ti-6Al-4V alloy for a given temperature and time, by inserting the activation energy of oxygen diffusion Q_d . In Figure 8.16, a plot of diffusion depth versus θ for temperatures 600 and 650°C, and times between 12-72 hours is given. This relation can be described by a power function as follows:

$$\text{ODZ Depth } (\mu\text{m}) = 3,1 \theta^{0,5} \quad (8.4)$$

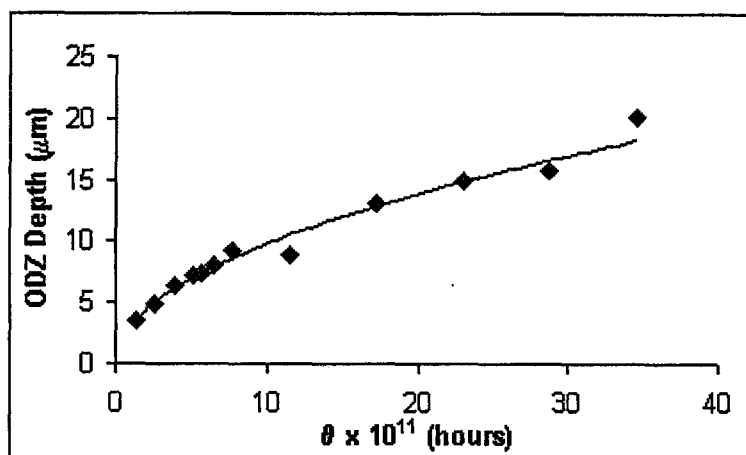


Figure 8.16. Variation of ODZ depth with temperature compensated time parameter θ .

The calculated ODZ depths obey the experimental data measured for the temperatures 700, 750 and 800°C and times between 6-48 hours with minor deviations from unity as shown in Figure 8.17.

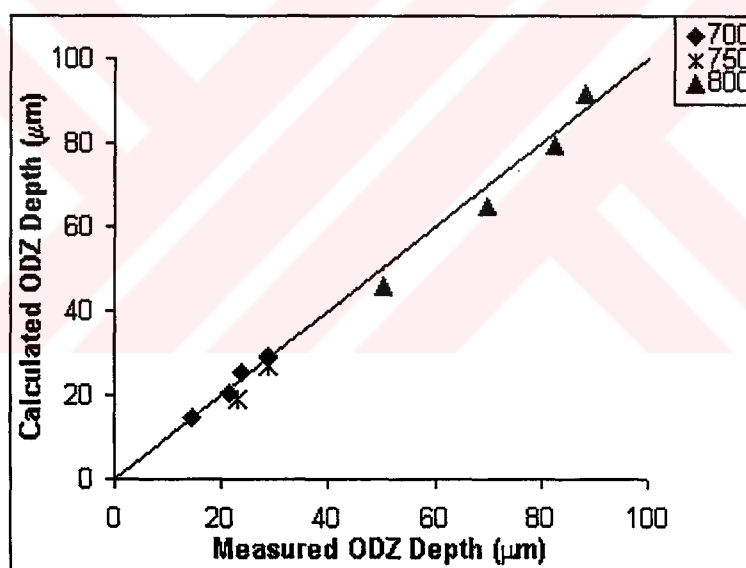


Figure 8.17. Plot of calculated versus measured ODZ depths for different temperatures and times.

8.5. Performance Tests

8.5.1. Corrosion Tests

Figure 8.18 presents the results of corrosion tests as weight loss of the samples with respect to duration time in 5 M HCl solution. Continuous dissolution of untreated alloy, which exhibited the lowest corrosion resistance among the investigated samples, was sustained throughout the testing period. Duration times of 12 and 36

hours achieved no measurable weight loss on the samples that were oxidized at 650°C. Prolonged corrosion tests resulted with abrupt increase in weight loss due to spallation of the oxide scales. For the samples oxidized at 600 C, weight loss gradually increased with increasing duration time. Longer times oxidation (60 and 72 hours) at 600C formed more protective surface layer, which did not show any weight loss for duration times of 12 h and 36 h. Among the investigated materials, the sample oxidized at 600 C for 60 h exhibited the maximum corrosion resistance.

Figure 8.19 shows the surfaces the samples after corrosion tests of 60 hours. In this figure white colored regions represent the bulk material while the oxides appeared black in color. The surface of the sample, which exhibited the maximum corrosion resistance, is still covered with oxide layer. Since the oxide layer is very effective in protecting the titanium and its alloys from the detrimental effects of corrosive media (Chapter 3.1) the higher the stability of the oxide layer the better is the corrosion resistance.

8.5.2 Wear Tests

Wear tests were carried out to compare the wear resistance of untreated alloy with that of the alloy oxidized at 600°C for 60 hours. As mentioned previously this oxidation condition provided maximum resistance to corrosion in 5 M HCl solution (Figure 8.16). Wear tests were performed under normal atmospheric condition and in 0.9 % NaCl solution. In this study the former is named as dry sliding wear and the latter is named as corrosion wear.

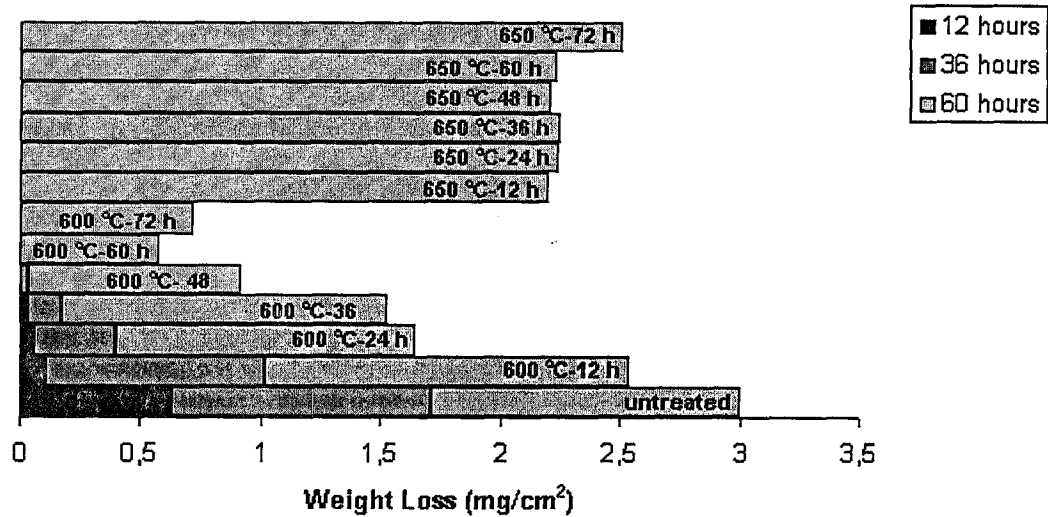


Figure 8.18. Weight loss data obtained through the immersion corrosion test conducted in 5 M HCl.

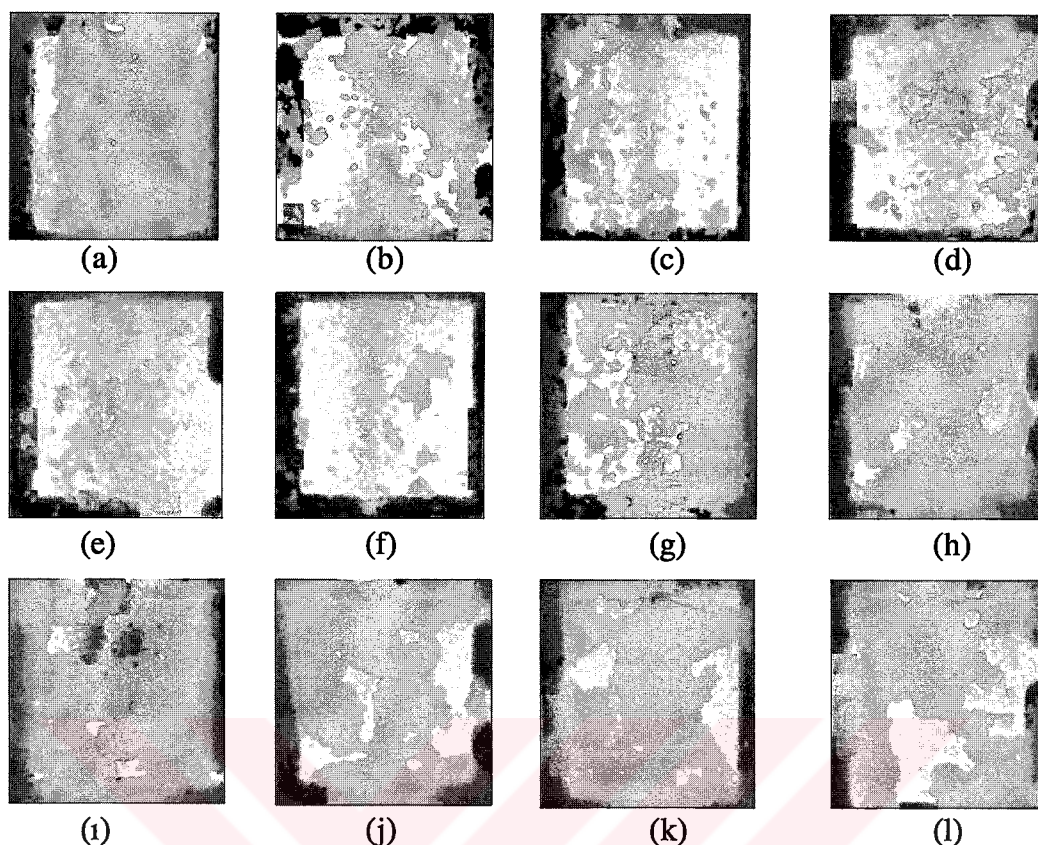


Figure 8.19 Photographs of surface appearances of oxidized samples after 60 hours corrosion testing; (a) 600°C-12 h, (b) 600°C-24 h, (c) 600°C-36 h, (d) 600°C-48 h, (e) 600°C -60 h, (f) 600°C -72, (g) 650°C -72,(h) 650°C -24, (i) 650°C -36, (j) 650°C-48 h, (k) 650°C-60 h, (l) 650°C-72 h.

The optical micrographs of the wear tracks developed on the surfaces of untreated and oxidized samples throughout dry sliding and corrosive wear tests are presented in Figure 8.20 and Figure 8.21. Wear tracks produced on oxidized surfaces exhibited different topography than the untreated surfaces. Typical feature of wear tracks produced on untreated surfaces is extensive shear deformation due to plowing action of Al_2O_3 ball. On oxidized surfaces wear progressed by deformation and removal of the asperities, which resulted with formation of white colored wear tracks. In dry sliding condition no measurable wear track depth was detected on the oxidized surface even after testing time of 300 minutes as seen in the 3-D profiles presented in Figure 8.22.

When compared to dry sliding wear, the wear of the oxidized sample progressed more rapid in corrosive environment. However, it was still more resistant than the untreated surface as depicted from the 3-D profiles in Figure 8.23. During

wear test of oxidized sample, smooth wear tracks were observed in the first 75 minutes, where thereafter wear progressed in the oxygen diffusion zone. Due to combination of mechanical and chemical effects, oxygen diffusion zone is removed after testing time of 225 minutes and by the end of test (300 minutes), base metal appeared in some regions of the wear track (Figure 8.21).

The results of reciprocating wear tests were quantified by measuring the cross-sectional areas of the wear tracks from their profiles at certain intervals of testing. As shown in Figure 8.22 and Figure 8.23 shallower and narrower wear tracks formed on oxidized surfaces than untreated ones.

Figure 8.24 clearly depicts that oxidation at 600°C for 60 hours provided excellent dry sliding and corrosion wear resistance to Ti-6Al-4V alloy. Especially, after dry sliding wear test the depth of the wear tracks formed on the oxidized surface could not be measured. (Figure 8.24 b) However, untreated alloy exhibited higher wear resistance in corrosive media than normal atmospheric condition (Figure 8.24 a). This situation could be the result of lubricative effect of 0.9 % NaCl solution. On the other hand, oxidized sample exhibited relatively high wear after testing time of 300 minutes in 0.9% NaCl solution, due to removal of oxide layer and oxygen diffusion zone.

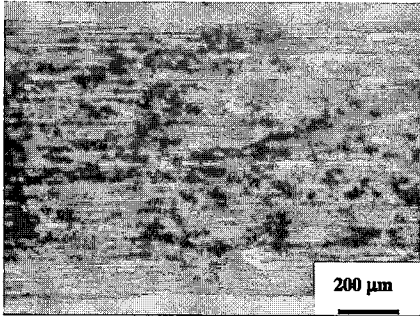
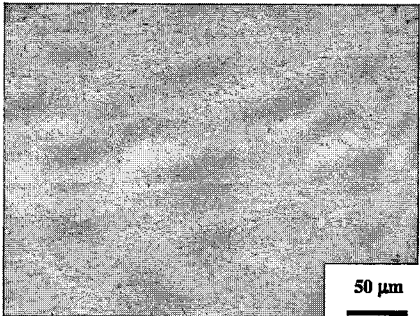
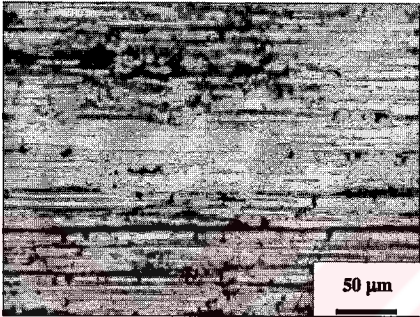
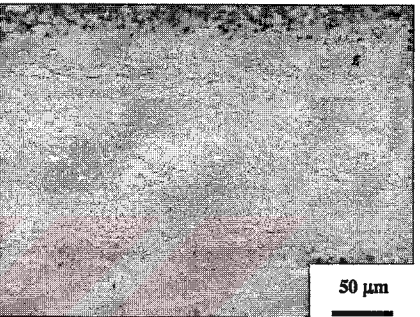
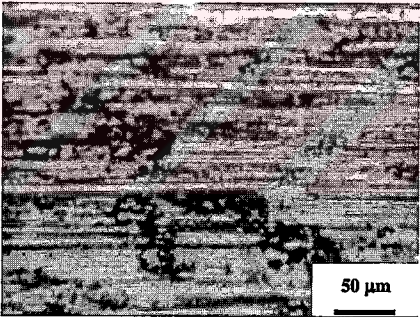
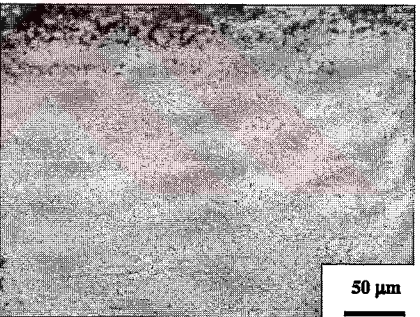
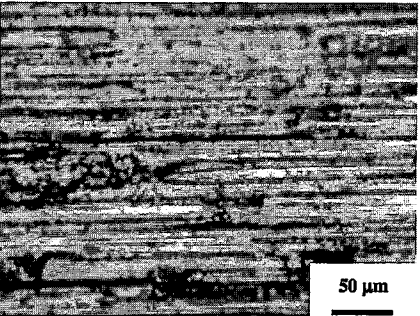
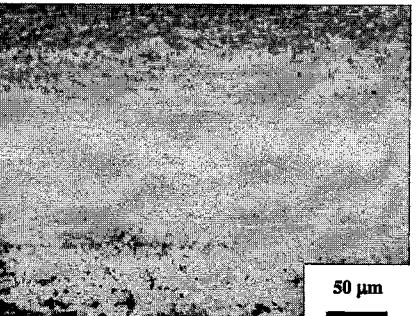
Test time	Untreated	Oxidized
45 minutes		
75 minutes		
225 minutes		
300 minutes		

Figure 8.20 Optical Micrographs of the dry sliding wear tracks formed on the surfaces of the untreated and oxidized (600° C-60 h) samples.

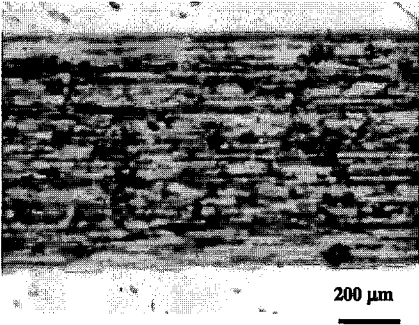
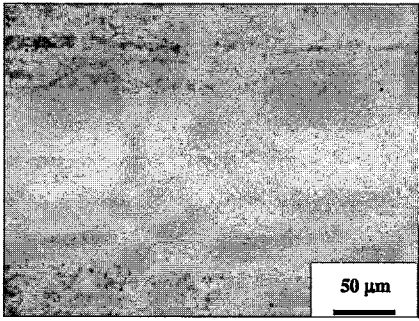
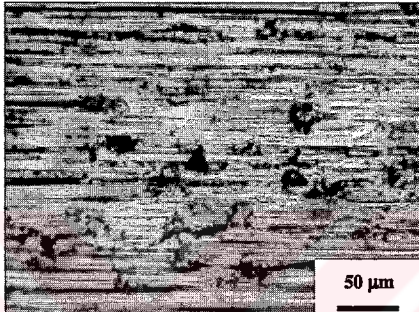
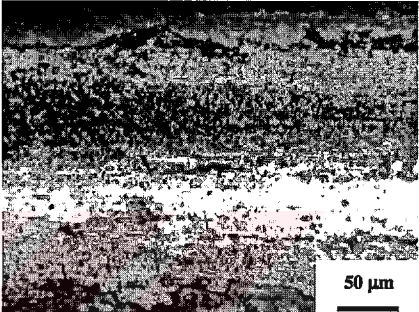
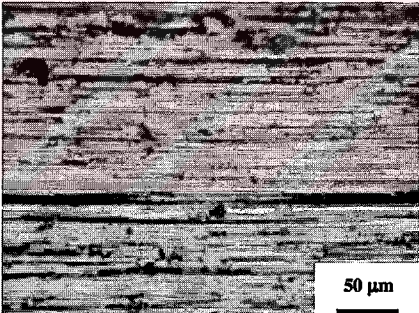
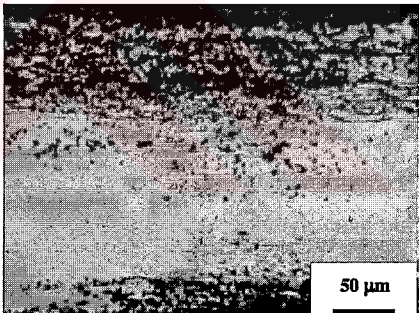
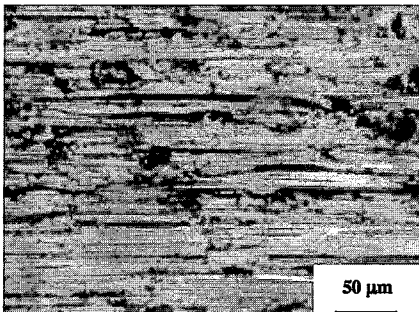
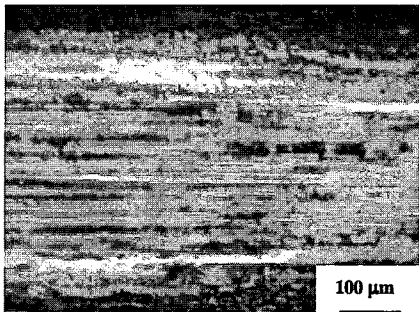
Test time	Untreated	Oxidized
45 minutes		
75 minutes		
225 minutes		
300 minutes		

Figure 8.21. Optical micrographs of the corrosion wear tracks of untreated and oxidized (600°C-60 h) sample.

The Al_2O_3 balls were also subjected to wear during testing of untreated and oxidized surfaces as shown in Figure 8.25. Optical microscopic examinations revealed that, wider and rougher worn surfaces form on the balls after sliding against the untreated surfaces when compared to those slide on oxidized surfaces. This suggests that particles of Al_2O_3 ball were pull – out from the surface during testing of untreated surfaces. Such pull out mechanism did not take place during testing of oxidized surfaces.

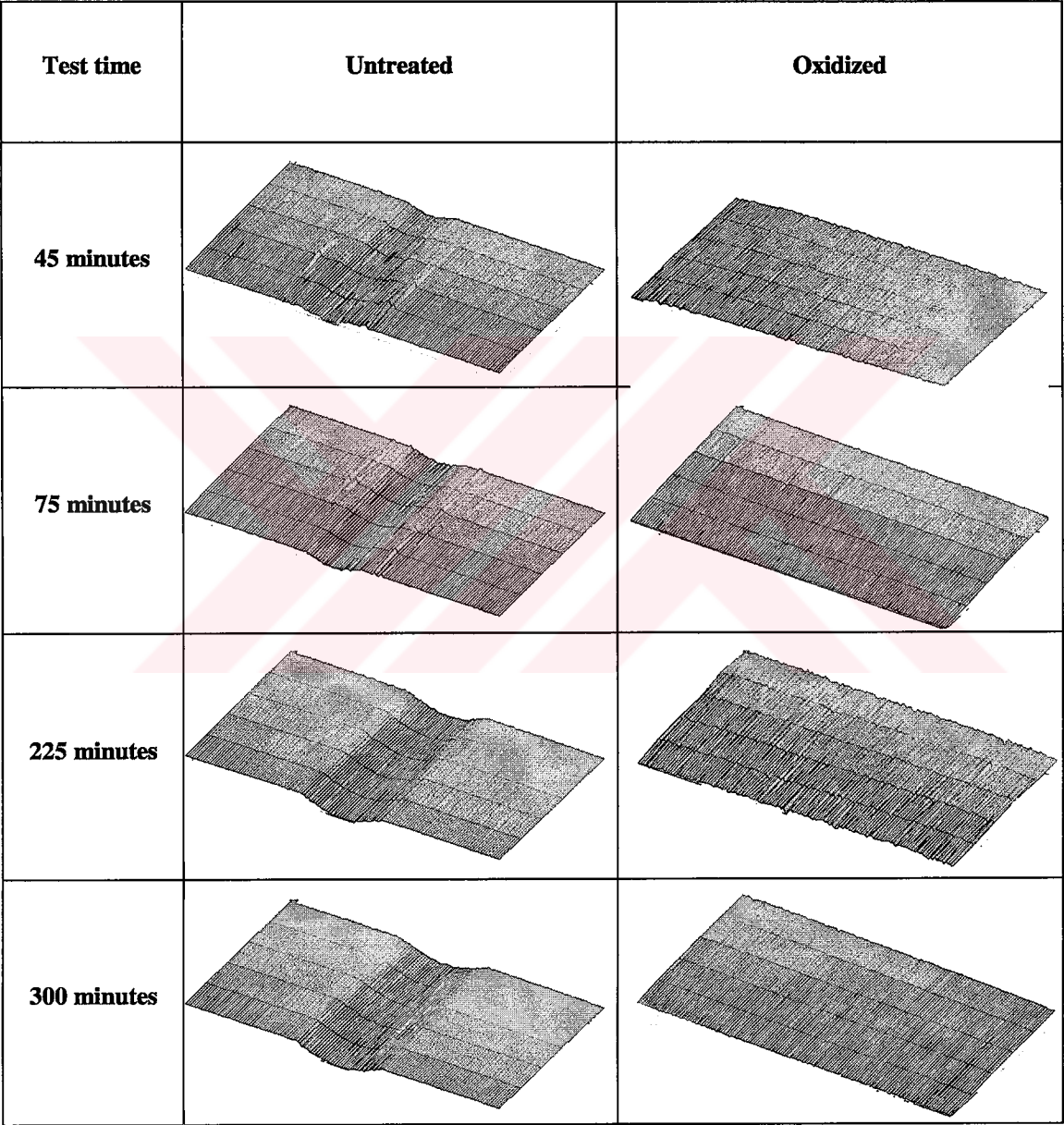


Figure 8.22 3-D surface profiles of untreated and oxidized samples after dry sliding wear

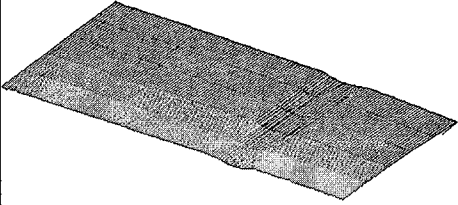
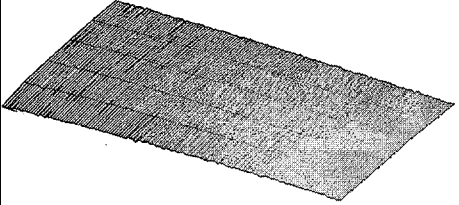
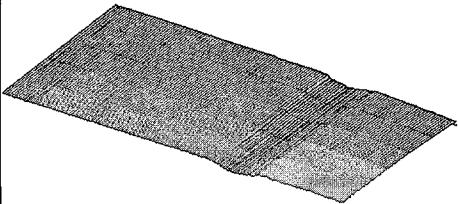
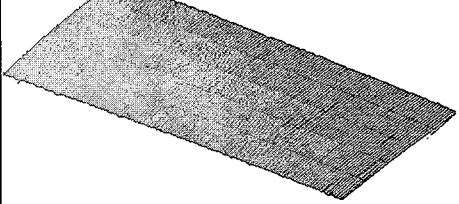
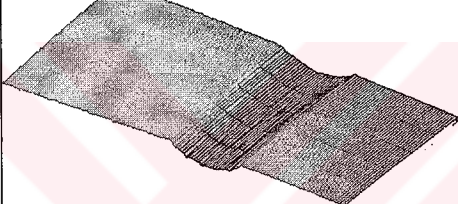
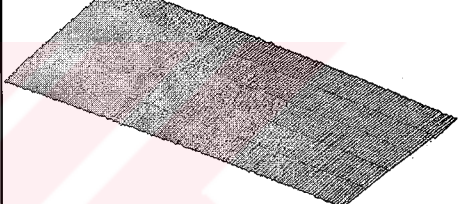
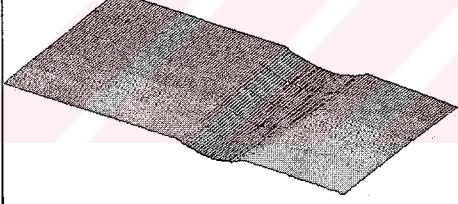
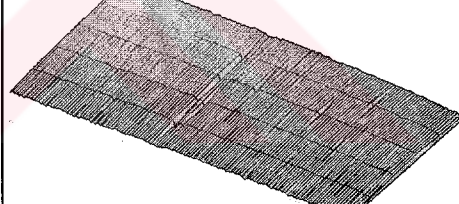
Test time	Untreated	Oxidized
45 minutes		
75 minutes		
225 minutes		
300 minutes		

Figure 8.23. 3-D surface profiles of untreated and oxidized samples after corrosion wear.

The areas of the wear scar formed on the contact surface of the ball are compared in Figure 8.26. In both dry sliding and corrosion wear conditions the wear of ball is severe for the untreated surface. In corrosion wear tests of oxidized surfaces relatively higher wear is observed on the ball with respect to dry sliding wear.

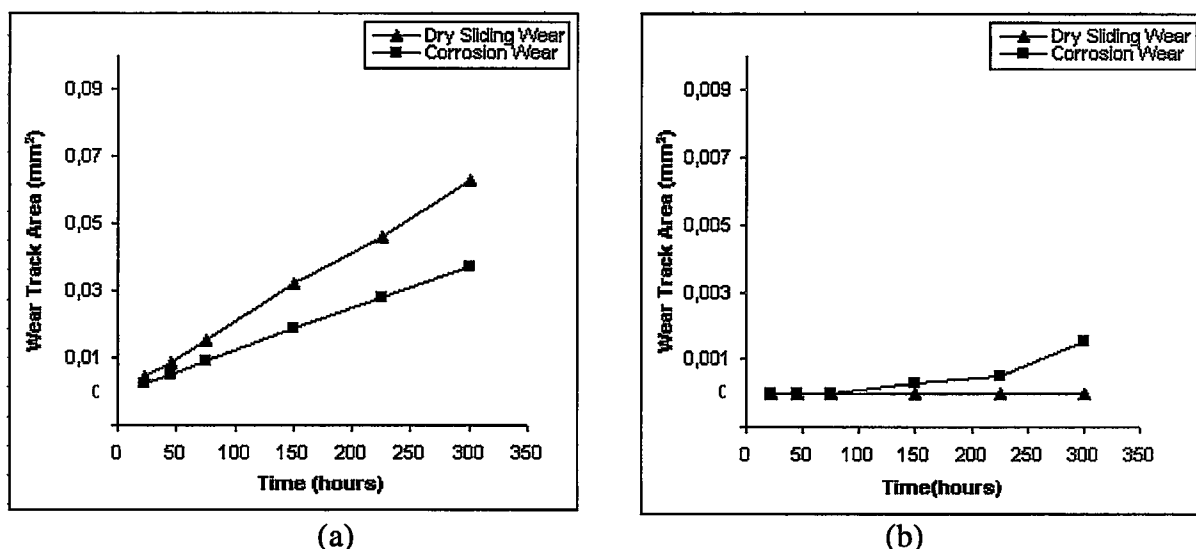


Figure 8.24. Progress of wear track areas for (a) untreated and (b) oxidized surfaces.

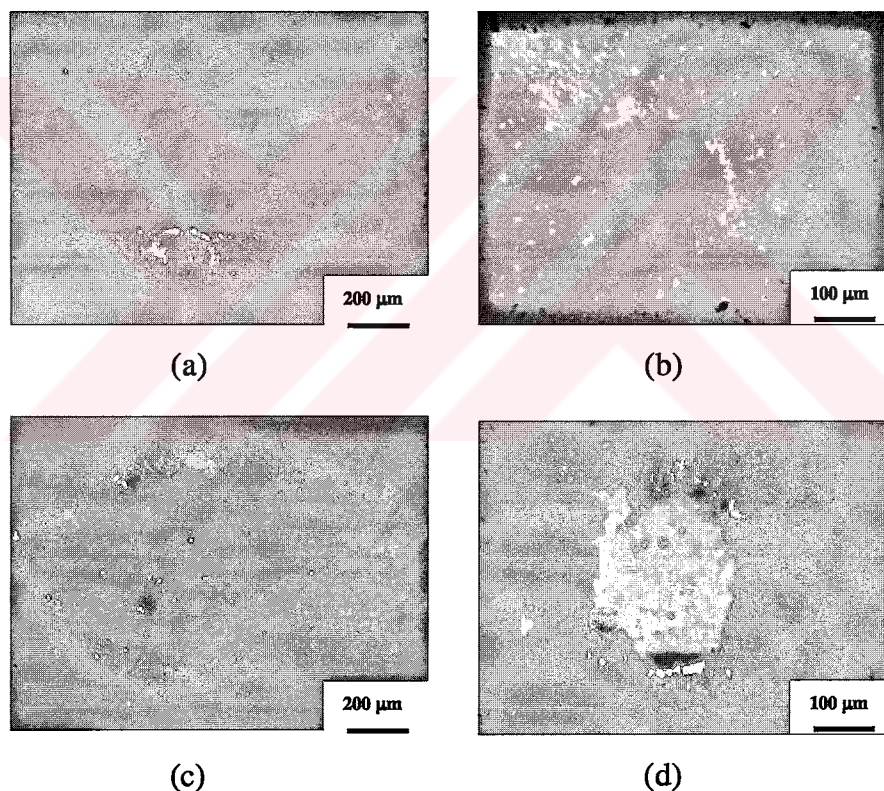


Figure 8.25. Wear scars that formed on the Al_2O_3 ball during (a) dry sliding against untreated surface, (b) dry sliding against oxidized surface, (c) corrosion wear against untreated surface, (d) corrosion wear against oxidized surface.

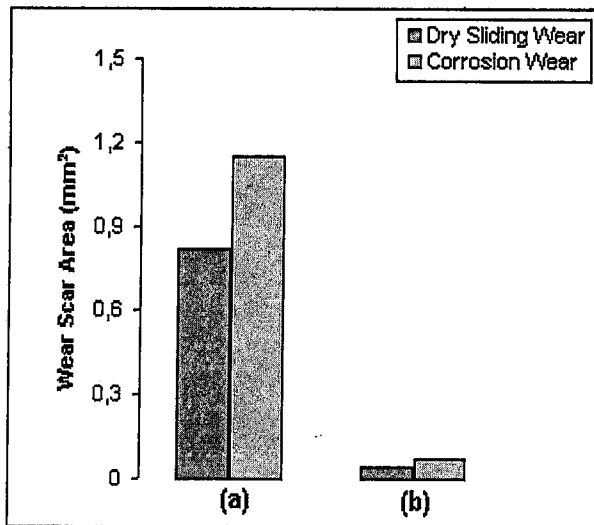


Figure 8.26. Areas of the wear scars that formed on Al_2O_3 balls when; (a) sliding on untreated sample surface, (b) sliding on oxidized surface.

9. CONCLUSION

Following conclusions can be drawn according to results of this study;

1. Thermal oxidation progressed by formation of an oxide layer composed of anatase and rutile, which are the different forms of TiO_2 , and a solid solution strengthened oxygen diffusion zone beneath the oxide layer. Upon increase of oxidation temperature and time, the thickness of the oxide layer and oxygen diffusion zone increased and rutile form of TiO_2 became more evident. In the examined Ti-6Al-4V alloy, modification of the surface by thermal oxidation increased the surface hardness from 3.5 GPa to 10 GPa and compressive residual stress from 3 GPa to 5.5 GPa.
2. Above oxidation temperature of 650°C oxide layers tended to crack and spall off, while they were not sufficiently thick below 600°C . Kinetic studies conducted on Ti-6Al-4V alloy oxidized at 600 and 650°C for various times up to 72 hours revealed that, oxidation activation energy and oxygen diffusion activation energies were 257 and 200 kJ/mol, respectively.
3. Thermal oxidation improved the corrosion resistance in 5 M HCl solution depending on the thickness of the oxide layer. Thick oxide layers exhibited excellent corrosion resistance for short duration times but extended duration times resulted with abrupt increase in corrosion rate due to spallation of the oxide scales. On the other hand thin oxide layers were not sufficiently protective against corrosive environment. The examined Ti-6Al-4V alloy exhibited excellent resistance to corrosion after oxidation at 600°C for 60 h.
4. Oxidation of Ti-6Al-4V alloy at 600°C for 60 hours improved both dry sliding and corrosion wear resistance. In 0.9 % NaCl solution, oxidized alloy exhibited 25 times higher wear resistance than untreated alloy. When compared to the results of dry sliding wear tests, on oxidized surfaces wear progressed relatively faster in 0.9 % NaCl solution.

REFERENCES

- [1] **Boyer, R., Welsch, G. and Collings, E.W.**, 1994. Materials properties handbook: Titanium alloys, ASM International, Materials Park, Ohio.
- [2] **Donachie, M.J.**, 1989, Titanium: A Technical Guide, ASM International, Metals Park, Ohio.
- [3] **Brunette, D.M., Tengwall, B., Textor, M. and Thomsen, P.**, 2001. Titanium in medicine, Springer Verlag, Heidelberg.
- [4] **Imam, M.A. and Fraker, A.C.**, 1996. Titanium alloys as implant materials, in Medical applications of titanium and its alloys, pp.3-15, Brown, S.A., Lemons, J.E., ASTM, Philadelphia.
- [5] **Dong, H. and Bell, T.**, 2000. Enhanced wear resistance of titanium surfaces by a new thermal oxidation treatment, *Wear*, **238**, 131-137.
- [6] **Long, M. and Rack, H.J.**, 1998. Titanium alloys in total joint replacement-a materials science perspective, *Biomaterials*, **19**, 1621-1639.
- [7] **Komotori, J., Lee, B.J., Dong, H. and Dearnley, P.A.**, 2001. Corrosion response of surface engineered titanium alloys damaged by prior abrasion, *Wear*, **88-98**, 1-11.
- [8] **Dearnley, P.A.**, 1999. A review of metallic, ceramic and surface-treated metals used for bearing surfaces in human joint replacements, Institution of Mechanical Engineers Proceedings, Part H, *Journal of Engineering in Medicine* **213**, 107-135.
- [9] **Boettcher, C., Bell, T. and Dong, H.**, 2002. Surface engineering of Timet 550 with oxygen to form a rutile-based, wear resistant coating, *Metallurgical and Materials Transactions A*, **33**, 1201-1211.
- [10] **Qi, P.-Y., Li, X.Y., Dong, H. and Bell, T.**, 2002. Characterization of the palladium-modified thermal oxidation-treated titanium, *Materials Science and Engineering A*, **326**, 330-342.
- [11] **Mishra, A.K., Davidson, J.A., Poggie, R.A., Kovacs, P. and FitzGerald, T.J.**, 1996. Mechanical and tribological properties and biocompatibility of diffusion hardened Ti-13Nb-13Zr-a new titanium alloy for surgical implants, in Medical applications of titanium and its alloys, pp.96-112, Brown, S.A., Lemons, J.E., ASTM, Philadelphia.
- [12] **Baboian, R.**, 1995. Corrosion Tests And Standarts: Application and Interpretation, ASTM Manual Series, Philadelphia.
- [13] **Bloyce, A., Qi, P.-Y., Dong, H. and Bell, T.**, 1998. Surface modification of titanium alloys for combined improvements in corrosion and wear resistance, *Surface and Coatings Technology*, **107**, 125-132.

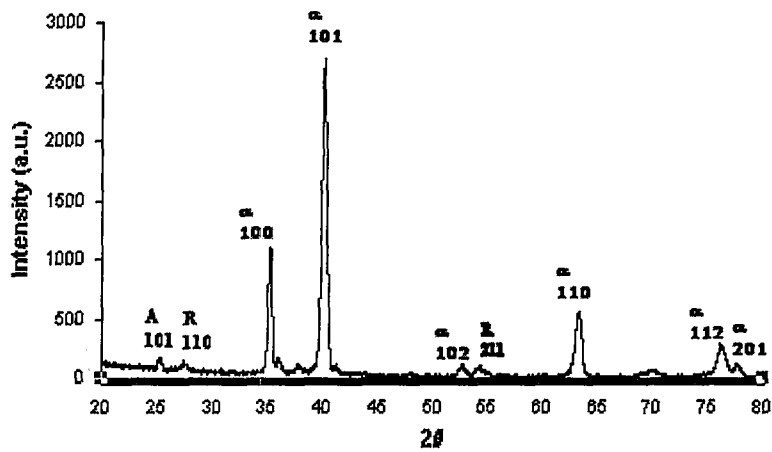
- [14] **Long, M. and Rack, H.J., 2001.** Friction and surface behavior of selected titanium alloys during reciprocating-sliding motion, *Wear*, **249**, 158-168.
- [15] **Dong, H. and Bell, T., 1999.** Tribological behavior of alumina sliding against Ti6Al4V in unlubricated contact, *Wear*, **225-229**, 874-884.
- [16] **Molinari, A., Straffelini, G., Tesi, B. and Bacci, T., 1997.** Dry sliding wear mechanism of the Ti6Al4V alloy, *Wear*, **208**, 105-112.
- [17] **Stachowiak, G.W. and Bachelor, A.W., 2001,** *Engineering Tribology*, Butterworth Heinemann, Boston.
- [18] **Rabinowicz, E., 1995.** *Friction and Wear of Materials*, Wiley Inc., New York.
- [19] **Galliano, F., Galvanetto, E., Mischler, S. and Landolt, D., 2001.** Tribocorrosion behavior of plasma nitrided Ti-6Al-4V alloy in neutral NaCl solution, *Surface Coatings and Technology*, **145**, 121-131.
- [20] **Dong, H., Bloyce, A., Morton, P.H. and Bell, T., 2001.** Surface oxidation of a titanium or titanium alloy article, United States Patent, No: 6,210,807, dated April 3, 2001.
- [21] **Dong, H., Bloyce, A. and Bell, T., 1999.** Slurry abrasion response of surface engineered Ti6Al4V ELI, *Tribology International*, **32**, 517-526.
- [22] **Dong, H. and Li, X.Y., 2000.** Oxygen boost diffusion for the deep-case hardening of titanium alloys, *Materials Science and Engineering A* **280**, 303-310.
- [23] **Wiklund, U. and Hutchings, I.M., 2001.** Investigation of surface treatments for galling protection of titanium alloys, *Wear*, **251**, 1034-1041.
- [24] **Garcia-Alonso, M.C., Saldana, L., Valles, G., Gonzalez-Garrasco, J.L., Gonzalez-Cabrero, J., Martinez, M.E., Gil-Garay, E. and Munuera, L., 2003.** In vitro corrosion behavior and osteoblast response of thermally oxidised Ti6Al4V alloy, *Biomaterials*, **24**, 19-26.
- [25] **Borgioli, F., Galvanetto, E., Galliano, F.P. and Bacci, T., 2001.** Air treatment of pure titanium by furnace and glow-discharge processes, *Surface Coatings and Technology*, **141**, 103-107.
- [26] **Lopez, M.F., Jimenez, J.A. and Gutierrez, A., 2003.** Corrosion study of surface-modified vanadium-free titanium alloys, *Electrochimica Acta*, **48**, 1395-1401.
- [27] **Kofstad, P., 1988.** *High Temperature Corrosion*, Elsevier Applied Science, Essex.
- [28] **Gobel, M., Haannappel, V.A.C. and Stroosnijder, M.F., 2001.** On the determination of diffusion coefficients of oxygen in one-phase Ti (α -Ti) and two-phase (α - and β -Ti) by micro-hardness measurement, *Oxidation of Metals*, **55**, 137-151.
- [29] **Weissman, S. and Shrier, A., 1968.** Strain distribution in oxidized alpha titanium crystals, in *The science, technology and application of titanium*, pp: 441-458, Jaffee, R.I., Promisel, N.E., Pergamon Press, London.

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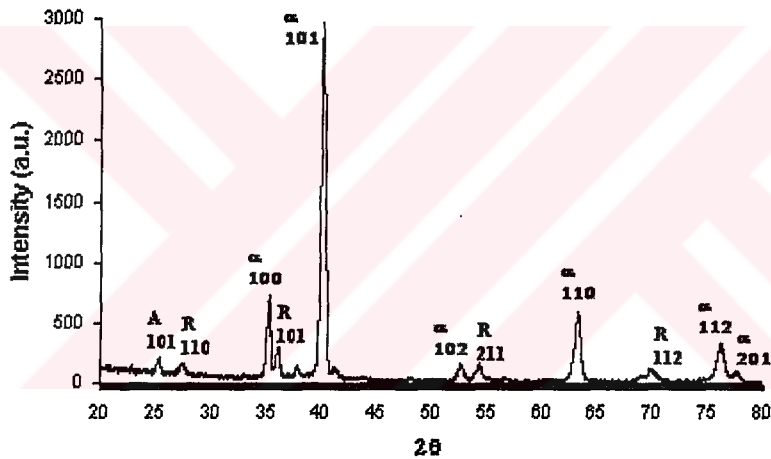
- [30] **Massalski, T.B., Okamoto, H., Subramanian, P.R. and Kaczprzak, L.,** 1990. Binary Alloy Phase Diagrams, ASM International, Materials Park, Ohio.
- [31] **Bertrand, G., Jarraya, K. and Chaix, J.M.,** 1983. Morphology of oxide scales formed on titanium, *Oxidation of Metals*, **21**, 1-19.
- [32] **Shamblen, J.E. and Redden, T.K.,** 1968. Air contamination and embrittlement of titanium alloys, in *The science, technology and application of titanium*, pp: 199-208, Jaffee, R.I., Promisel, N.E., Pergamon Press, London.
- [33] **Frangini, S. and Mignone, A.,** 1994. Various aspects of the air oxidation behaviour of a Ti6Al4V alloy at temperatures in the range 600-700°C, *Journal of Materials Science*, **29**, 714-720.
- [34] **Du, H.L., Datta, P.K., Lewis, D.B. and Burnell-Gray, J.S.,** 1994. Air oxidation behaviour of Ti-6Al-4V alloy between 650 and 850°C, *Corrosion Science*, **36**, 631-642.
- [35] **Unnam, J., Shenoy, R.N. and Clark, R.K.,** 1986. Oxidation of commercial purity titanium, *Oxidation of Metals*, **26**, 231-252.
- [36] **Chaze, A.M. and Coddet, C.,** 1987. Influence of alloying elements on the dissolution of oxygen in the metallic phase during the oxidation of titanium alloys, *Journal of Materials Science*, **22**, 1206-1214.
- [37] **Chatterjee, U.K., Bose, S.K. and Roy, S.K.,** 2001. *Environmental Degradation of Metals*, Marcel Dekker Inc., New York.
- [38] **Imbrie, P.K., and Lagoudas, D.C.,** 2001. Morphological evolution of TiO₂ scale formed on various 1D and 2D geometries of titanium, *Oxidation of Metals*, **55**, 359-399.
- [39] **Krishnamurthy, R. and Srolovitz, D.J.,** 2003. Stress distributions in growing oxide films, *Acta Materiala*, **51**, 2171-2190.
- [40] **Garbacz, H. and Lewandowska, M.,** 2003. Microstructural changes during oxidation of titanium alloys, *Materials Chemistry and Physics*, (Article in Press, Corrected proof).
- [41] **Hoepfner, D.W. and Chandrasekaran, V.,** 1996. Characterizing the fretting fatigue behaviour of Ti-6Al-4V in modular joints, in *Medical applications of titanium and its alloys*, pp.252-265, Brown, S.A., Lemons, J.E., ASTM, Philadelphia.
- [42] **<http://www.materials.qmw.ac.uk/casestud/implants>**
- [43] **<http://www.hipsandknees.com>**
- [44] **Wright, T.M. and Goodman, S.B.,** 2001. *Implant Wear in Total Joint Replacement: Clinical & Biologic Issues, Material & Design Considerations*, American Academy of Orthopaedic Surgeons, Illinois.
- [45] **ASTM G31 – 72,** 1995. Standard practice for laboratory immersion corrosion testing of metals, ASTM, Philadelphia.

- [46] **Coddet, C., Chaze, A.M. and Beranger, G., 1987.** Measurement of the adhesion of thermal oxide films: application to the oxidation of titanium, *Journal of Materials Science*, **22**, 2969-2974.
- [47] **Zhang, X.D., Evans, D.J., Baeslack III, W.A. and Fraser, H.L., 2003.** Effect of long term aging on the microstructural stability and mechanical properties of Ti-6Al-2Cr-2Mo-2Sn-2Zr alloy, *Materials Science and Engineering A*, **344**, 300-311.
- [48] **Zhang, X.D., Wiezorek, J.M.K., Baeslack III, W.A., Evans, D.J. and Fraser, H.L., 1998.** Precipitation of ordered α_2 phase in Ti-6-22-22 alloy, *Acta Materiala*, **46**, 4485-4495.
- [49] **Kunert, M., Baretzky, B., Baker, S.P. and Mittemeijer, E.J., 2001,** Hardness-depth profiling on nanometer scale, *Metallurgical and Materials Transactions A*, **32**, 1201-1209.
- [50] **Suresh, S. and Giannakopoulos, A.E., 1998.** Anew method for estimating residual stresses by instrumented sharp indentation, *Acta Materiala*, **46**, 5755-5767.
- [51] **Atar, E., Sarioglu, C., Demirler, U., Kayali, E.S. and Cimenoglu, H., 2003.** Residual stress estimation of ceramic thin films by X-ray diffraction and indentation techniques, *Scripta Materiala*, **48**, 1331-1336.
- [52] **Hertzberg, R.W., 1983.** *Deformation and Fracture Mechanics of Engineering Materials*, John Wiley and Sons, Inc., New York.

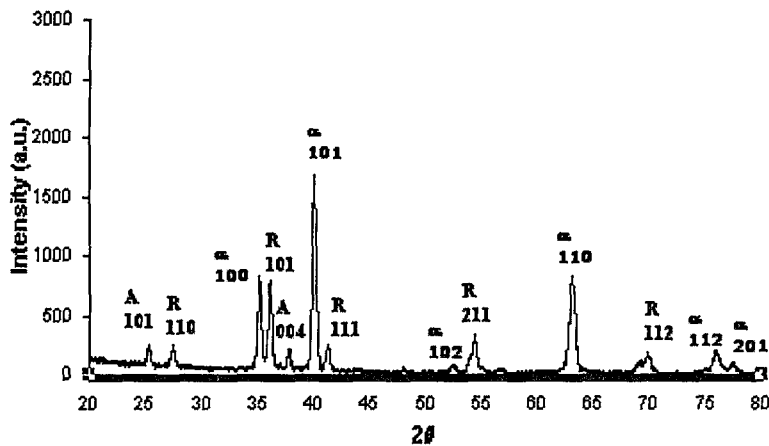
APPENDIX



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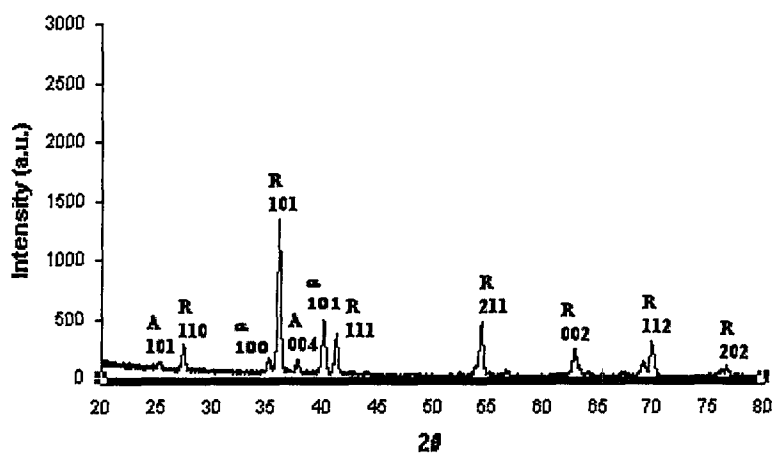


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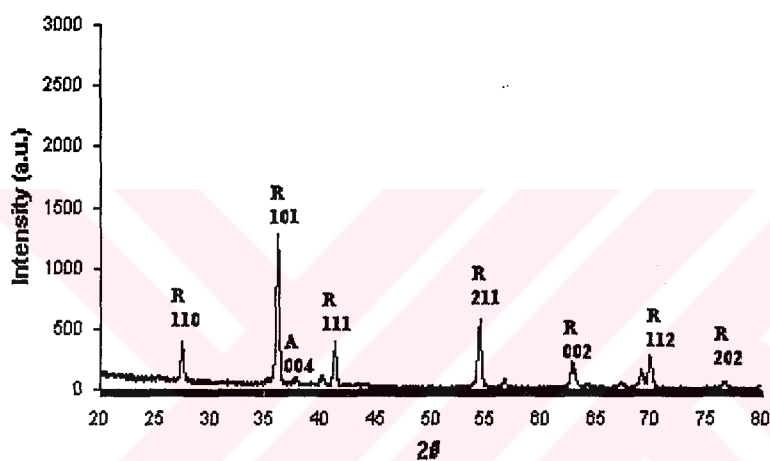


(c)

Figure A.1. XRD patterns oxidized surfaces after oxidation at 600°C (a) 12 hours, (b) 24 hours, (c) 48 hours (α: hcp titanium, A: anatase, R: rutile).

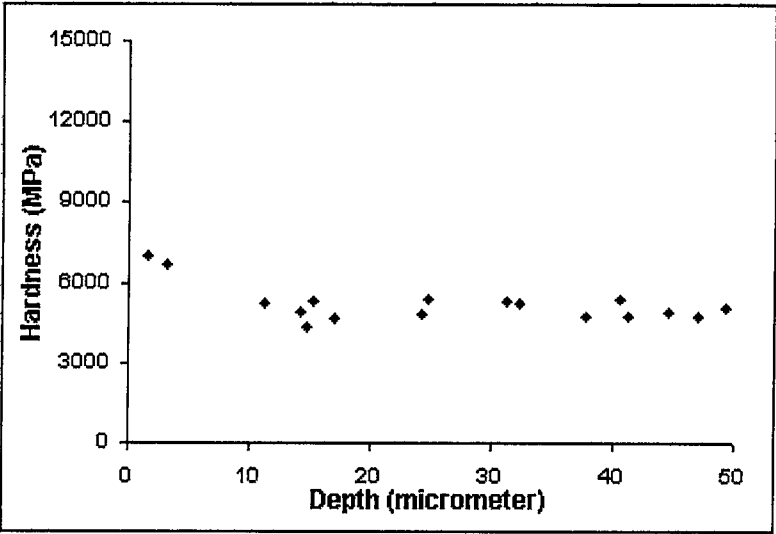


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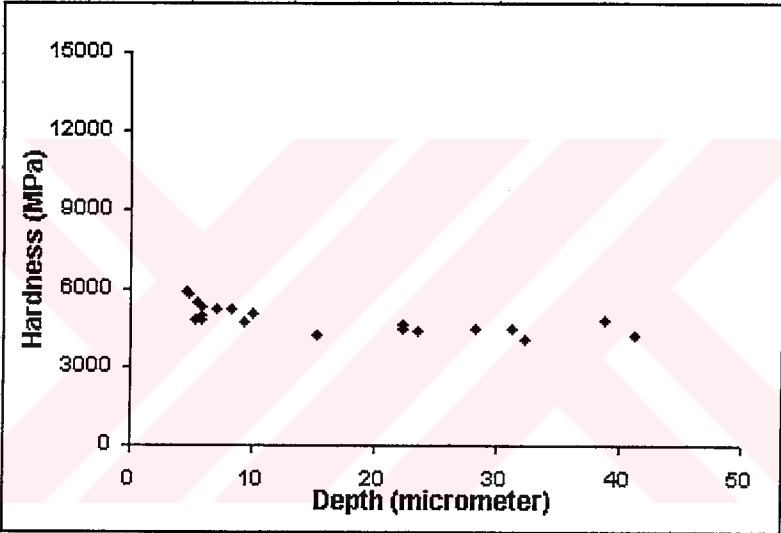


(b)

Figure A.2. XRD patterns of oxidized surfaces after oxidation at 650°C (a) 24 hours, (b) 48 hours(α: hcp titanium, A: anatase, R: rutile).

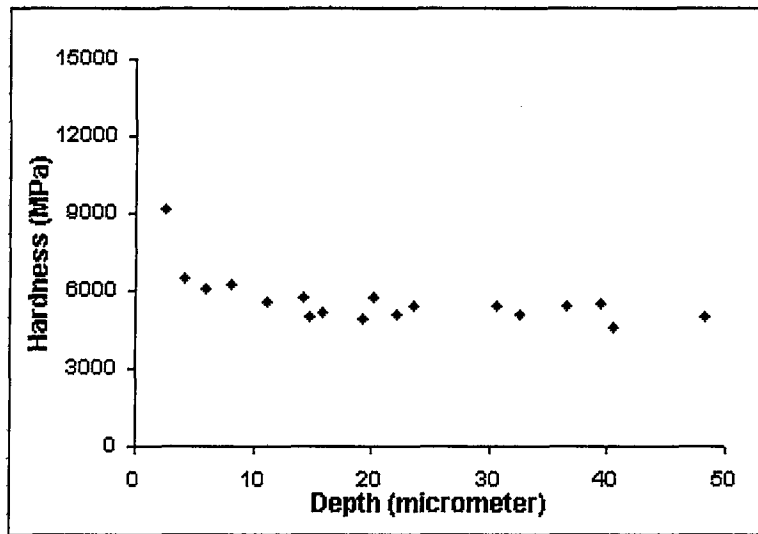


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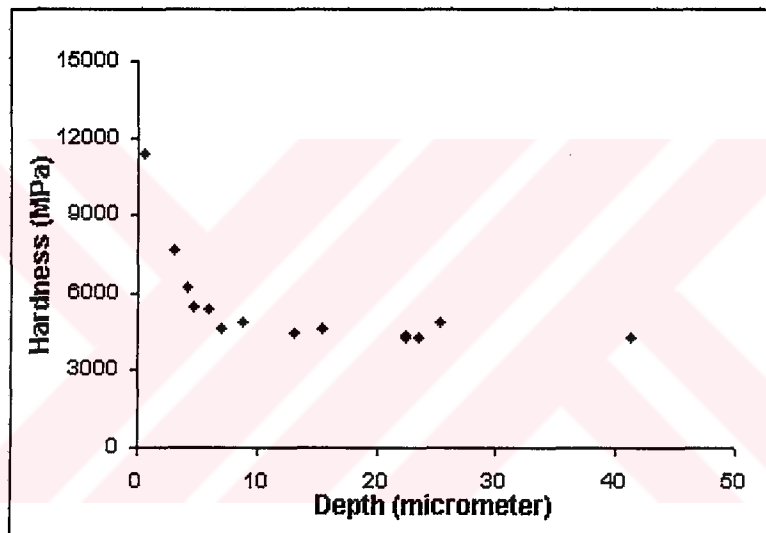


(b)

Figure A.3. Hardness- depth profiles of oxygen diffusion zones after oxidation at 600°C (a) 12 hours, (b) 24 hours.

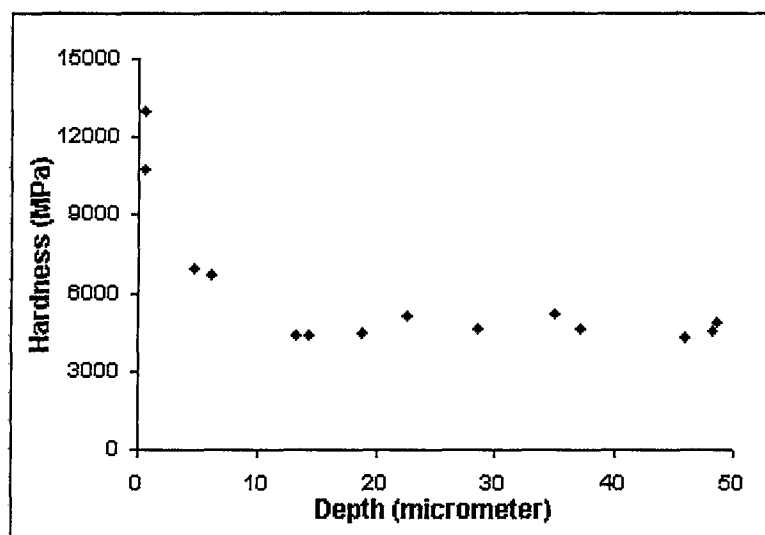


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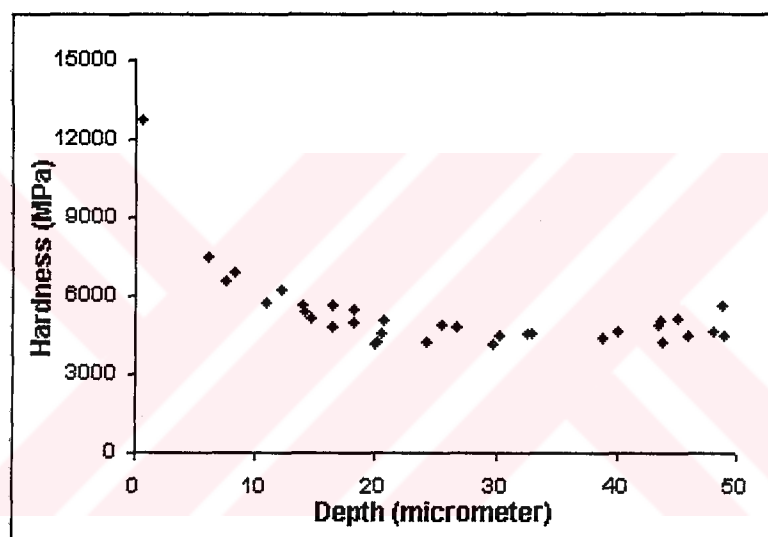


(b)

Figure A.4. Hardness - depth profiles of oxygen diffusion zones after oxidation at 600°C (a) 36 hours, (b) 48 hours.

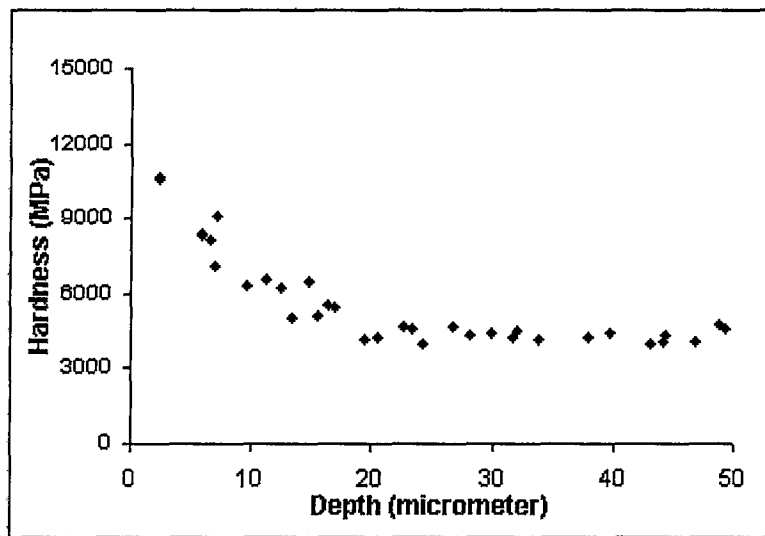


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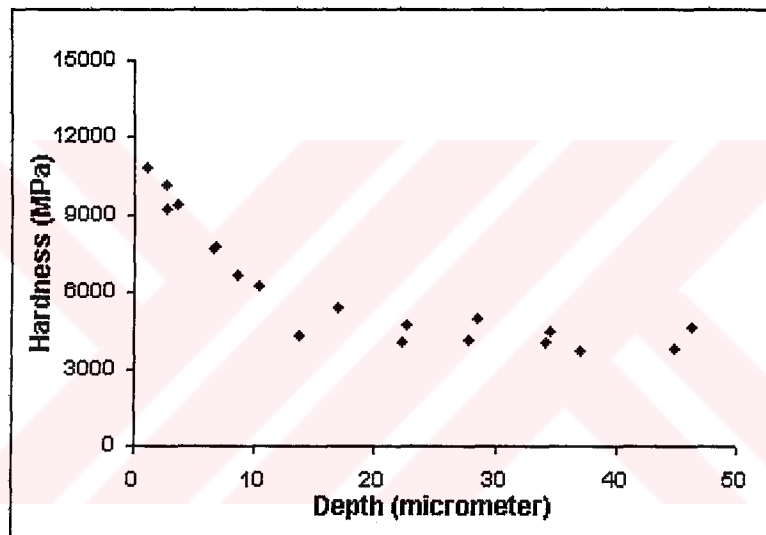


(b)

Figure A.5. Hardness - depth profiles of oxygen diffusion zones after oxidation at 650°C (a) 12 hours, (b) 24 hours.



(a)



(b)

Figure A.6. Hardness - depth profiles of oxygen diffusion zones after oxidation at 650°C (a) 36 hours, (b) 48 hours.

BIOGRAPHY

Hasan Gülerytiz was born in Sinop, Turkey in 1975. He graduated from the Beşiktaş Atatürk Anadolu High School in 1993 and entered Metallurgical and Materials Engineering Department of Istanbul Technical University in 1994. He was honoured the degree of B.Sc. in 2001. He started his graduate study at the Institute of Science and Technology in the Materials Science and Engineering Programme of Advanced Technologies in Engineering Science Programme at the Istanbul Technical University. He is being supported by the The State Planning Organization of Turkey for his graduate study.

