# Oxidation kinetics of commercially pure titanium

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## ABSTRACT

The aim of this work was to perform thermal characterization of commercially pure titanium in dry air to determine its oxidation kinetics and the structure of the oxide. The oxidation kinetics were determined thermogravimetrically under isothermal conditions in the temperature range 300 to 750 $^o$C for 48 hours and the structure of the oxides was determined by differential thermal analyses and X-ray diffraction in the temperature range room temperature - 1000 $^o$C. The oxidation rate of titanium increased with increase in temperature. It was high in the initial stages of oxidation and then decreased rapidly with time, especially up to 600 $^o$C. The kinetic laws varied between inverse logarithmic at the lower temperatures (300 and 400 $^o$C) and parabolic at the higher temperatures (650, 700 and 750 $^o$C). Evidences from X-ray diffraction and differential thermal analyses data revealed that the passive oxide film formed at room temperature crystallized into anatase at about 276 $^o$C. The crystallized oxide formed in the range 276 - 457 $^o$C consisted of anatase, in the range 457 – 718 $^o$C consisted of anatase and rutile sublayers, and at temperatures beyond 718 $^o$C consisted of a layer of pure rutile. Scanning electron microscopy observations reveled that the oxidized surfaces were crack-free and the surface roughness increased steadily with oxidation temperature.

**Keywords:** Titanium, oxidation kinetics, oxide film, structure.

# Cinética de oxidação de um titânio puro comercial

## RESUMO

O objetivo deste trabalho foi de realizar uma caracterização térmica de um titânio puro comercial para estudar sua cinética de oxidação e seus produtos de corrosão formados em atmosfera de ar seco em função da temperatura. A cinética de oxidação foi determinada por termogravimetria em condições isotérmicas entre 300 e 750 $^o$C por 48 horas e os óxidos formados foram caracterizados por análise térmica diferencial e difração de raios-X entre a temperatura ambiente até 1000 $^o$C. A cinética de oxidação aumenta com a temperatura e é muito rápida nos primeiros instantes, diminuindo rapidamente com o tempo, especialmente até 600 $^o$C. As leis cinéticas variaram entre a logarítmica inversa nas temperaturas mais baixas (300 e 400 $^o$C) e a parabólica nas temperaturas mais altas (650, 700 e 750 $^o$C). As análises por difração de raios-X e análise térmica diferencial mostraram que a cristalização do filme passivo de óxido, formado naturalmente à temperatura ambiente, ocorre aproximadamente a 276 $^o$C. A estrutura do óxido é composta de anatásia cristalina entre 276 e 457 $^o$C, anatásia e rutilo entre 457 e 718 $^o$C, e somente rutilo acima de 718 $^o$C. Observações por microscopia eletrônica de varredura revelaram que as superfícies oxidadas não apresentam fissuras e que suas rugosidades aumentam uniformemente com a temperatura de oxidação.

**Palavras-chave**: Titânio, cinética de oxidação, filme de óxido, estrutura.

## 1    INTRODUCTION

The biocompatibility of titanium or its alloys is attributed to the oxide film formed on the material [1-3]. This oxide film promotes a good osseointegration and prevents the dissolution of metallic ions into the surrounding tissue [4]. Cell proliferation and mechanical interlocking between the implant and the bone depend on the morphology and composition of the oxide layer [5, 6]. Nevertheless, the characteristics of the oxide film depend on the chemical composition, structure, morphology and mechanical conditions of the implanted material. Many surface treatments have been proposed to improve the biological performance of

the implants. Among these techniques, the oxidation of titanium has been investigated recently [7]. The oxidation can be enhanced by thermal oxidation or by micro-arc oxidation, also known as plasma electrolysis [5, 8]. This process is performed by applying a positive voltage to a titanium specimen immersed in an electrolyte (anodic oxidation). When the applied voltage is increased to a certain point, a micro-arc occurs as a result of the dielectric breakdown of the $TiO_2$ layer. At this moment, Ti ions in the implant and OH ions in the electrolyte move in opposite directions very quickly to form $TiO_2$ again [7, 8]. Recent studies demonstrated that this treatment increases the thickness and roughness of the oxide layer, which leads to a beneficial effect on the biocompatibility of the titanium implants [7].

When the titanium is exposed to ambient air at room temperature, a passive oxide film is spontaneously formed on its surface. This passive film is amorphous, very thin (5-10 nm thickness [9]), and composed of three layers [10, 11]: the first layer adjacent to metallic titanium is TiO, the intermediary layer is $Ti_2O_3$, and the third layer, which is in contact with the environment, is anatase $TiO_2$. At room temperature, anatase $TiO_2$ is the most important layer in thickness and responsible for the integration between the implant and the human bone when the material is not submitted to a thermal treatment at high temperature. The surface oxide film on titanium formed in the air is so protective that the further oxidation of titanium is prevented in various circumstances and mediums [12]. Even during sterilization in autoclave under a saturated water vapor pressure at 120 $^o$C for 1.8 ks, oxidation of titanium does not proceed [12].

Oxidation at high temperatures promotes the development of a crystalline oxide film. Increasing temperature induces the formation of a thicker oxide layer, which is accompanied with dissolution of oxygen beneath it [13]. Feng and $al.$ [14] investigated the oxidation of a commercially pure titanium at 600 $^o$C for 30 min. in air, in the oxygen and in the water vapor with 1.13-1.15 Pa. Surface composition and crystal structure analyses carried out by X-ray photoelectron spectroscopy (XPS) and by X-ray diffraction (XRD), respectively, indicated that titanium was oxidized in every medium, and formed films of rutile $TiO_2$ instead of anatase $TiO_2$ [14]. Nevertheless, thermal oxidation at 600 $^o$C and 650 $^o$C for 48 h at normal atmospheric condition revealed that the oxidized surfaces of the Ti-6Al-4V alloy principally consist of rutile but the anatase form of $TiO_2$ was also detected at limited number of diffraction angles, especially after oxidation at 600 $^o$C (13). However, at 650 $^o$C rutile totally dominated the oxide structure [13].

Although some works have reported the structure of the oxide film in many temperatures, none of them have investigated the crystallization temperature of the passive oxide film and the stability domain of anatase and rutile as a function of temperature. In this paper, a systematic study has been carried out to evaluate the oxidation kinetics and the transition temperatures of each oxide phase formed on commercially pure titanium.

## 2    MATERIALS AND METHODS

Samples of commercially cast titanium were gradually polished up to 1 μm alumina, cleaned in ethanol, and dried at room temperature. The average chemical composition, measured by X-Ray fluorescence spectroscopy (Shimadzu RF-5301), was found to be Ti – 0.078 wt.% Fe – 0.065 wt.% Mn – 0.026 wt.% Zn. Oxidation kinetics of this material were performed by thermogravimetry between 300 and 750 $^o$C for 48 h in dry air with an accuracy of $10^{-6}$ g. Characterization of the oxide films was made by differential thermal analyses (DTA), X-ray diffraction (XRD), and scanning electron microscopy (SEM). Thermogravimetry (TG) and DTA tests were carried out on disks of 5 mm diameter and 2 mm thickness with a Netzsch equipment (Jupiter STA 449C). DTA was performed in dry air between room temperature and 1000 $^o$C at a heating speed of 5 $^o$C/min. Samples of 20 mm x 17 mm x 2 mm were oxidized in a furnace, at normal atmospheric conditions, for 48 h between 200 and 800 $^o$C. After oxidation, a XRD-6000 Shimadzu X-ray diffractometer was used to identifier the oxides formed on the titanium. $CuK_\alpha$ radiation source was used and the incidence beam scan was 2$^o$/min. Diffraction angle range was between 10$^o$ and 80$^o$, with a step increment of 0.02$^o$ and a count time of 0.6 s.

## 3    RESULTS AND DISCUSSIONS

### 3.1    Oxidation Kinetics

Figure 1 shows that the oxidation kinetics are very fast in the beginning of the oxidation and decrease gradually with time within the firsts 10 and 20 minutes. The steady state is reached after a short time and depends on the oxidation temperature. At lower temperatures (300 and 400 $^o$C) the weight gain per surface unity (mg/cm$^2$) is very low and the oxide film oxidized in inverse ratio of the logarithmic law. At 650, 700 and 750 $^o$C the oxidation kinetics are parabolics and at 500 and 600 $^o$C the oxide film grows somehow between a parabolic and an inverse logarithmic law. As a matter of fact, the oxidation kinetics are very close to a paralinear law. Nevertheless, the weight gain remains relatively low up to 600 $^o$C.

## 3.2    Differential Thermal Analyses and X-ray Diffraction

Figure 2 shows the transformations of the oxide film during the heating. The peak at 73,5 °C is due to volatilization of ethanol molecules adsorbed on the surface of the passive film. At 276.1 °C the passive film converted to a crystalline film. The next transformation is observed at about 444-470 °C (peak at 457.2 °C). Evidences from XRD have shown a crystalline film of anatase between these two peaks (Figure 3). The major peak of anatase was found at $2\theta = 38.1°$. Actually, between 276 and 500 °C there are a double peak composed of anatase ($2\theta = 38.1°$) and titanium ($2\theta = 38.3°$). A systematic investigation between 200 and 300 °C confirmed that the transition between the passive film to a crystalline film of anatase might occur at approximately 275 °C. At this temperature the oxide film is very thin and the peaks observed by XRD are from titanium substrate. At 300 °C the anatase peak can be clearly detected by XRD (Figure 4). At approximately 444 °C (peak at 457 °C) rutile begins to nucleate and then the oxide film is constituted of anatase and rutile sublayers (Figure 2). The peak at 680-730 °C (718 °C ) indicates that anatase is no longer stable, converting to rutile, which is the only stable oxide above 718 °C. This results are also back up by XRD, which indicates that the oxide film formed at 500 and 600 °C is constituted of anatase and rutile, and at 700 and 800 °C rutile totally dominated the oxide structure (Figure 3). At 700 °C a slight peak of anatase was identified after 48 of oxidation showing that the reaction needs more time or higher temperatures to complete the transformation. The peak at 900 °C, which starts at about 885 °C, is due to the allotropic transformation of αTi to βTi (Figure 2). Allotropic transformation of pure titanium is reported to be at 882,5°C as a result of a new atomic structure arrangement, from hexagonal (α phase) at room temperature to cubic (β phase) between 882,5°C and its melting point at 1670 °C [15].
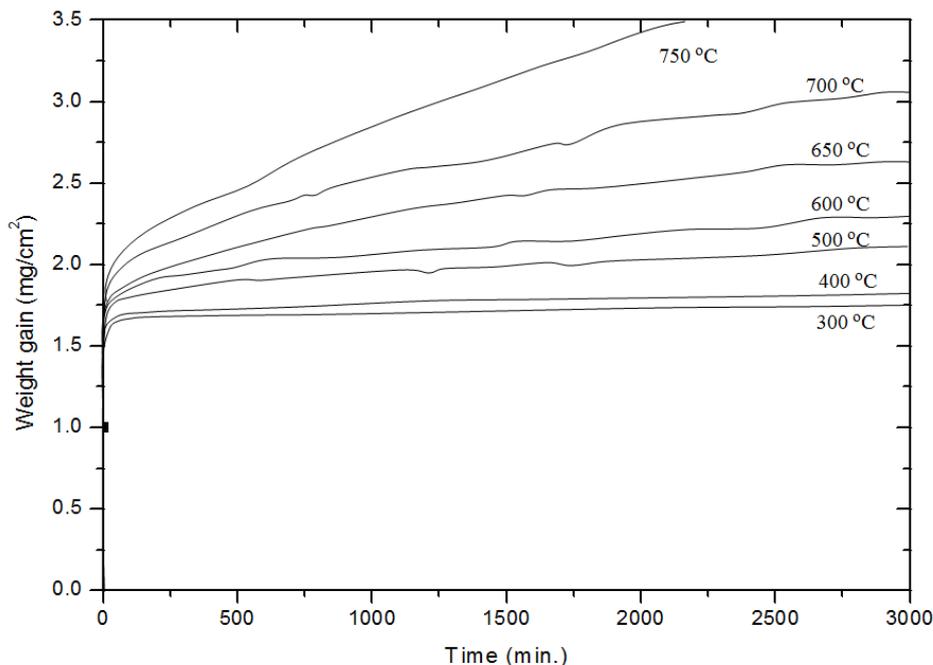


**Figure 1**: Isothermal oxidation kinetics of titanium in dynamic air atmospheres.
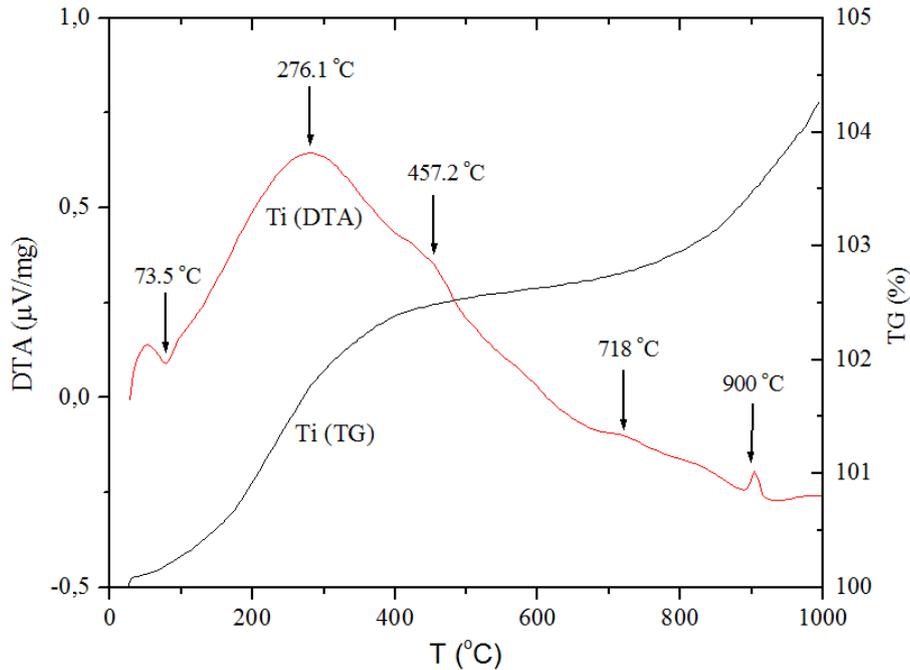
**Figure 2**: TG and DTA curves of titanium.

The formation of defective oxide structure after crystallization provides easier diffusion paths for oxygen and/or titanium ions allowing oxidation progress with temperature. At 300 and 400 $^o$C the oxide film is very thin and the matter transport is influenced by the electric field formed between the internal (metal/film) and the external (film/air) interfaces. Therefore, migration of the ionic species is predominant leading to an oxidation kinetic that corresponds to the well known Cabrera and Mott's model, i.e. the oxide film grows according to the inverse logarithmic law. At 650 $^o$C diffusion takeovers the migration and the oxidation kinetic is controlled by diffusion of the species through the oxide layer. Therefore, an intermediary mechanism is speculated at 500 and 600 $^o$C, which could explain the oxidation kinetics observed in Figure 1. At these temperatures the oxide film is still somewhat thin and the migration due to the electric field might play an important role along with the diffusion that is improved by the crystallization, which creates easier diffusion paths through the grain boundaries. The large peak at 276.1 $^o$C (Figure 2) also represents the oxidation energy, i.e. at low temperatures (200 - 400 $^o$C) the reaction is very fast leading to a thicker layer which increases steady and very slowly between 400 $^o$C and 700 $^o$C. Over 700 $^o$C the reaction is accelerated again as we can observe in the TG curve (Figure 2). This result shows that the oxide film is very effective against corrosion up to 700 $^o$C. From this temperature the oxide film growth is stimulated by diffusion as a result of temperature and oxide structure. Nevertheless, the effect of the oxide structure is overlapped by the temperature effect and it is still unclear whether or not the rutile structure is less effective than anatase to prevent matter transport in the scale.
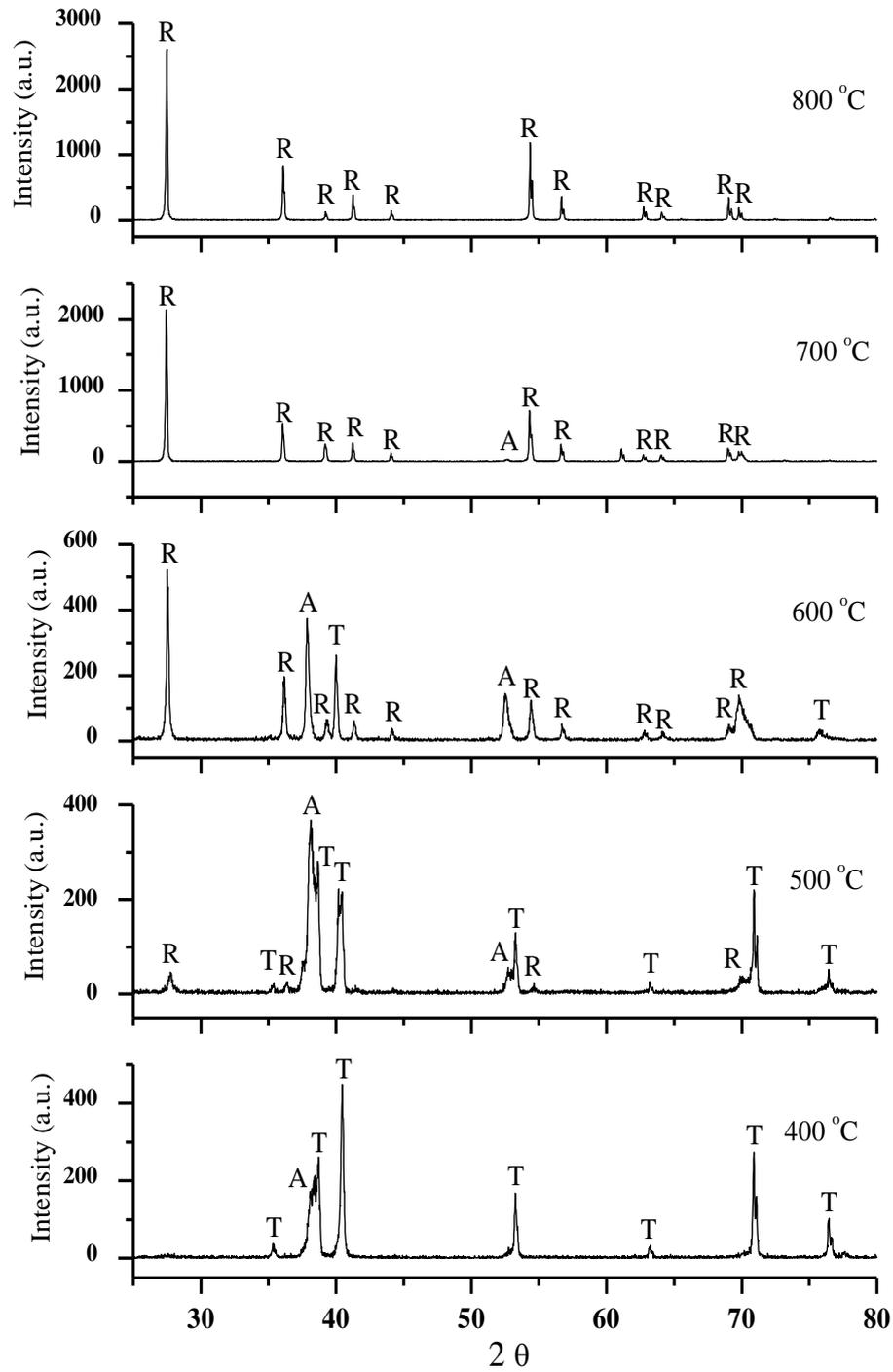
**Figure 3**: XRD patterns of titanium surfaces oxidized 48 hours in air (T = titanium, A = anatase, R = Rutile).
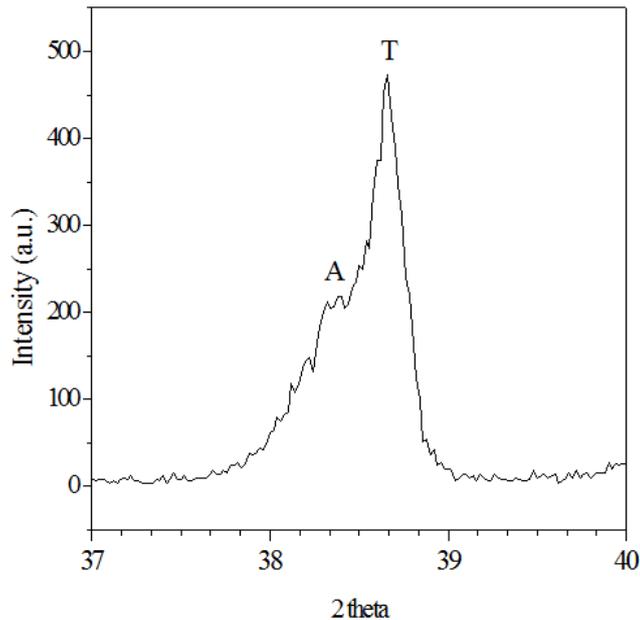
**Figure 4**: XRD patterns showing the crystallization of the passive film of titanium surfaces oxidized 48 hours at 300 $^o$C in air (T = titanium, A = anatase).

SEM observations on top of the oxide films showed that the surfaces are crack-free and uniformly roughness, which increases with the oxidation temperature (Figure 5). The surface roughness, measured on the Ti-6Al-4V according to average roughness (Ra) values, which define the arithmetic mean of departure of a surface profile from a mean line, indicated that the roughness of oxidized surfaces at 600 and 650 $^o$C for 48 h was 0,80 and 1,35 μm, respectively [13]. Average roughness of untreated sample was 0.17 μm before oxidation [13].
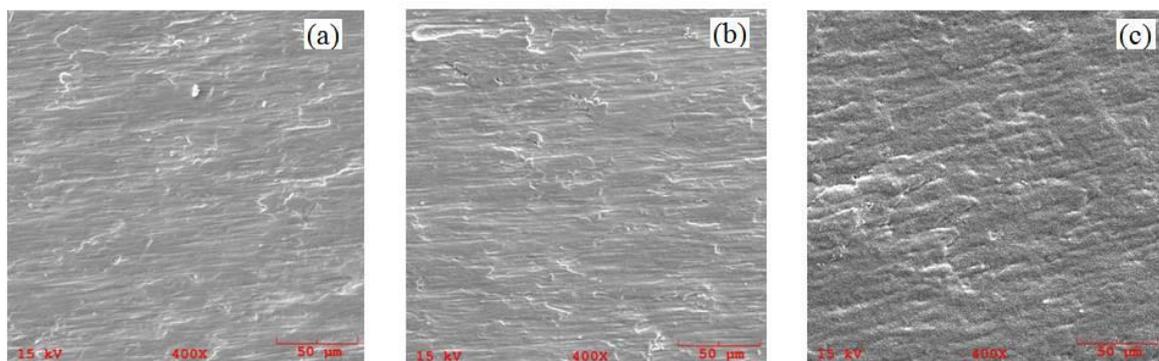


**Figure 5**: SEM micrographs of surface appearances of oxidized samples for 48 h in dry air at 300 $^o$C (a), 500 $^o$C (b) and 700 $^o$C (c).

## 4    CONCLUSION

Commercially pure titanium was thermally characterized up to 1000 $^o$C. Oxidation reaction is very fast in the early stages of the oxidation process leading to oxide layers composed of anatase and rutile structures of $TiO_2$. After the initial period, the oxidation kinetics are very slow up to 650 $^o$C due to the excellent thermal behavior of the scale. Crystallization of the passive film into anatase occurs at about 276 $^o$C. Rutile starts growing from about 444 $^o$C (peak at 457 $^o$C). Between 457 and 718 $^o$C the oxide film is composed of anatase and rutile sublayers. After 718 $^o$C the oxide layer is constituted of rutile only. Oxidation kinetics and SEM analysis have shown that the oxide film formed on the titanium is very effective against corrosion, crack-free and uniformly roughness.

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