# THE EFFECT OF THERMAL OXIDATION OF POROUS AND NON-POROUS TITANIUM ALLOY

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**Abstract**

One of the most important two-phase alloys α+β is Ti-6Al-4V, which is frequently used in medicine. This alloy is characterized by innovative combination of strength, good corrosion resistance in the environment of chlorides, the highest biotolerance and the lowest Young's modulus. Ti-6Al-4V is the basic material for long-life implants in orthopaedics, traumatic surgery, dentistry or cardiology. Taking into account current level of technology and operating methodologies, the use of metal biomaterials remains to be necessary. However, technological progress causes an increase interest in development of new materials with the possibility of stimulation for osseointegration. The metallic and ceramic sintered are numbered among multi-phase materials and are considered as materials with functional properties, such as increased resistance to fracture toughness and porosity, very good biocompatibility compared to other metallic biomaterials and fatigue strength. Modification of the surfaces of engineering materials especially titanium alloys is intended to improve function and usability these materials (e.g. good corrosion resistance in the environment of human tissues) [1-2]. The composites for analysis were obtained using the most modern methods of powder sintering i.e. spark plasma sintering (SPS). The main aim of the study was to evaluate the surface morphology of the alloy and functional properties after the thermal oxidation at different temperatures. The results of optical microscope metallography, SEM/EDX, XRD analysis are also presented.

**Keywords:** Metallic and ceramic sintered, Ti-6Al-4V, Titanium alloy, surface modification

## 1. INTRODUCTION

Metallic-ceramic composites are considered as materials with functional properies, what makes them very attractie for a application as materials for medicine. Therefore, the medical environments envourages the research on new composites made of ceramics, polymers and metallic materials [3-5]. Titanium and its alloys are the most modern and prospective implantation materials for biomedical applications. The above alloys were initially designed for the aerospace, marine, chemical and automotive industries, only after some time they have been modernized and used as titanium biomaterials [6].

Titanium and titanium alloys are very attractive and long-life materials for a number of biomedical devices and components, e.g. orthopedic and dental implant. The use of Ti-6Al-4V is constantly growing due to unique functional properties, such as good corrosion resistance, good biocompatibility, relatively low modulus, good fatigue strength [7-8]. Taking into account, that not all titanium and its alloys can meet all of the clinical requirements, a number of research centres have focused their efforts on surface modification in order to improve some properties. This is particularly relevant in case of e.g. porous titanium alloys, which without any surface treatmens is bioinert [9-10].

In order to improvement in homogeneity of titanium oxide layer and for increasing resistance to biological impact of the environment have used thermal oxidation, which is a low-cost, effective and relatively simple method of surface modification. This modification has brought a formation of a stable and protective layer of titanium dioxide ($TiO_2$) that avoids direct contact between the implants and its environment and also reduces the reactivity of the metal. The main factors on the performance of oxidized layer are the thermal oxidation temperature and time [11-13].

The authors of the present study proposed to improve functional properties by means of thermal oxidation at range of temperatures 400-600°C. $TiO_2$ amorphous phase crystallized in anatase phase at temperatures above 400°C, while the transformation of anatase to rutile was occured at temperatures around 600°C. The above reaction depends on the preparation conditions, surface area, porosity and crystal size [14-15]. The suitable surface treatment increase the use of titanium and titanium alloys in the biomedical sectors. The layer of titanium dioxide may relief in reduces the friction coefficient and so increase the wear resistance. The main aim of the study was to evaluate the effect of thermal oxidation on the structure and functional properties on titanium alloy Ti-6Al-4V manufactured by means of powder sintering methodology (spark plasma sintering, SPS).

## 2. MATERIALS AND METHODS

The specimes for the examinations with height of 5 mm and 25 mm in diameter were cut out from a bar of bulk titanium alloy 100% Ti-6Al-4V ELI. **Table 1** presents chemical composition of Ti-6Al-4V ELI. The second set of samples (porous sinters) containing of 100% Ti-6Al-4V powder were obtained using the spark plasma sintering method in an SPS HP 5 (FCT) device in a shielding gas medium at the pressure of 20 MPa. The samples were compressed in 1000°C with the force of 11 kN and a piston moving rate of 1 mm/s. Bulk density of powders (Sulzer Metco) of titanium alloy Ti-6Al-4V with spherically-shaped particles (size -45+5 μm) is 2.96 $g/cm^3$.

**Table 1** Chemical composition of Ti-6Al-4V ELI (% wt.)

| Chemical composition | Al | V | C | Fe | O | N | H | Ti |
|---|---|---|---|---|---|---|---|---|
| Ti-6Al-4V | 5.94 | 4 | 0.01 | 0.17 | 0.1 | 0.01 | <0.01 | Balance |

In view of recommended surface treatment for titanium alloys used in implantology, all samples were polished until bright finish. The next stage was thermal oxidation for 1 hour at temperatures: 400ºC, 500ºC, 600ºC.

Analysis of microstructure before and after thermal oxidation was conducted using the optical microscope Axiovert 25 and scanning microscope Jeol JSM-6610LV.

X-ray phase analysis using a X-ray diffractometer Seifert 3003 was carried out with the following parameters: supply voltage 30kV, current intensity 40 mA, measurement step 0.01º, channel integration time 10s; characteristic radiation wavelength for a cobalt lamp coordinated with a nickel filter 0.17902 nm.

## 3. RESULTS AND DISCUSSION

**Figure 1** presents the microstructure obtained for titanium alloys by the optical microscope Axiovert 25.

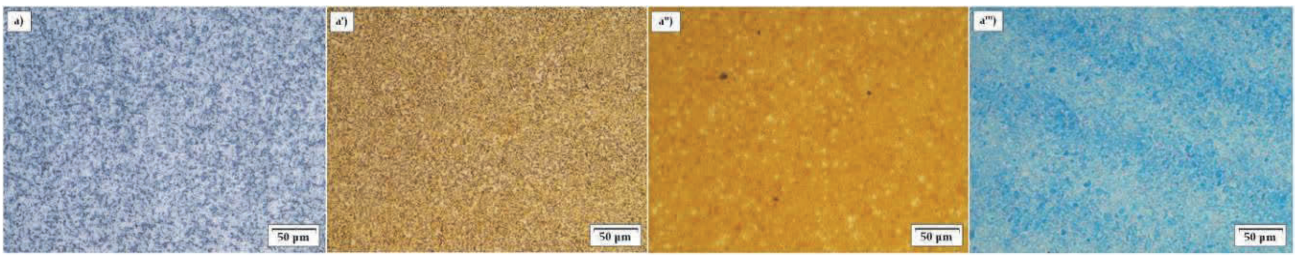



**Figure 1a** Microstructure of the titanium alloy 100% Ti-6Al-4V (bulk alloy): a) before thermal oxidation and after thermal oxidation at temperatures: a') 400ºC, a'') 500ºC, a''') 600ºC

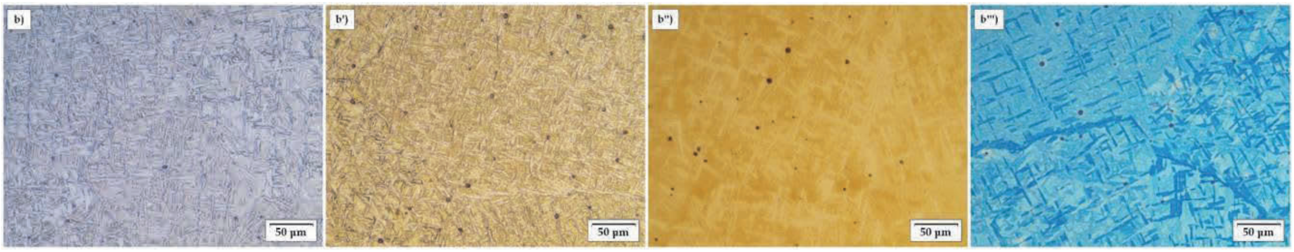



**Figure 1b** Microstructure of the porous sinters 100% Ti-6Al-4V (25 MPa): b) before thermal oxidation and after thermal oxidation at temperatures: b') 400ºC, b'') 500ºC, b''') 600ºC

**Figure 2** represents the examples of macroscopic images for titanium alloys after thermal oxidation.

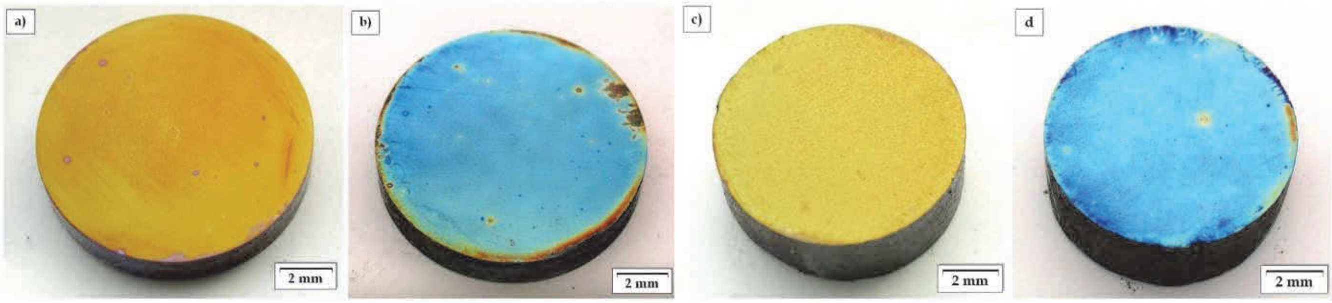



**Figure 2** Macroscopic images of the titanium alloys after thermal oxidation at appropriate temperatures: a) 100% Ti-6Al-4V (bulk alloy) at 500ºC, b) 100% Ti-6Al-4V (bulk alloy) at 600ºC, c) 100% Ti-6Al-4V (porous sinters) at 500ºC, d) 100% Ti-6Al-4V (porous sinters) at 600ºC

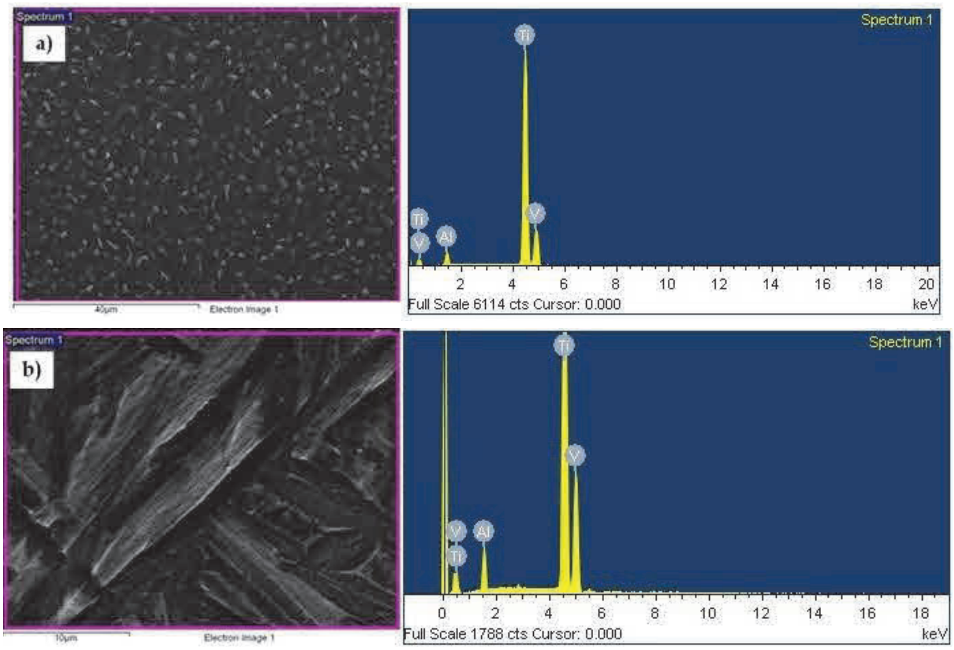



**Figure 3** Analysis of chemical composition (Spectrum 1): a) 100% Ti-6Al-4V (bulk alloy) after thermal oxidation at temperature 400ºC, b) 100% Ti-6Al-4V (porous sinters) after thermal oxidation at temperature 500ºC

The examples of SEM microstructure and EDS spectra of the titanium alloys after thermal oxidation obtained by the scanning microscope Jeol JSM-6610LV are presented in **Figure 3**. **Table 2** presents analysis of chemical composition of the above titanium alloys.

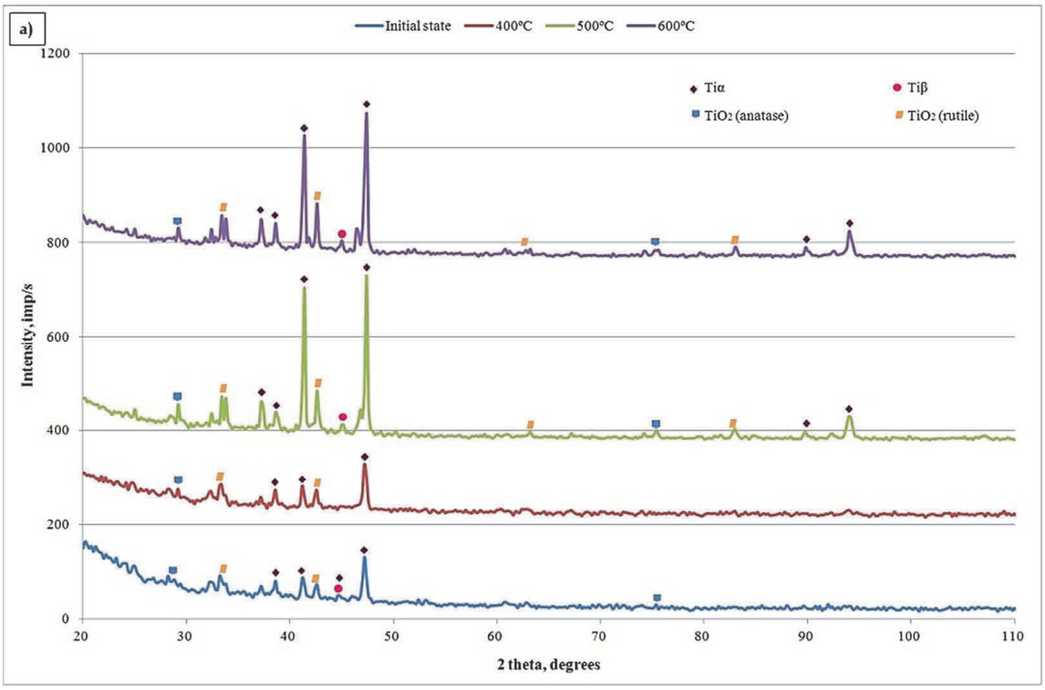
**Table 2** EDX-analysis of chemical composition of the titanium alloys after thermal oxidation at appropriate temperatures

| Titanium alloy | Temperature of thermal oxidation [ºC] | Element (weight %) | | | |
|---|---|---|---|---|---|
| | | Ti | V | Al | O |
| 100% Ti-6Al-4V (bulk alloy) | 400 | 90.18 | 3.98 | 5.84 | - |
| | 500 | 84.04 | 3.81 | 5.15 | 6.99 |
| | 600 | 75.16 | 3.57 | 4.20 | 17.07 |
| 100% Ti-6Al-4V (porous alloy) | 400 | 90.90 | 3.63 | 5.47 | - |
| | 500 | 89.90 | 4.29 | 5.82 | 8.98 |
| | 600 | 77.45 | 3.37 | 4.67 | 14.51 |

Analysis of chemical composition revealed that the higher oxidation temperatures determine the increase in oxide concentration on the surface.

Results of the analysis of phase composition of the titanium alloys are presented in **Figure 4**.

The phase composition analysis for specimens of 100% Ti-6Al-4V (bulk alloy) and 100% Ti-6Al-4V (porous sinters) revealed presence the peaks from the alpha titanium that crystallizes in a hexagonal crystallographic lattice (P63/mmc) with the following parameter: a = b = 0.295 nm, c = 0.468 nm and the beta titanium that crystallizes in a cubic crystallographic lattice (Im-3m) with the following parameter: a = b = c = 0.330 nm. The phase composition analysis revealed presence the peaks from the oxide $TiO_2$ anatase that crystallizes in a tetragonal crystallographic lattice ($P4_2$/mnm) with the following parameter: a = b = 0.378 nm, c = 0.951 nm. Furthermore, the phase composition analysis revealed presence the peaks from the oxide $TiO_2$ rutile that crystallizes in a tetragonal crystallographic lattice ($I4_1$/amd) with the following parameter: a = b = 0.459 nm, c = 0.296 nm.



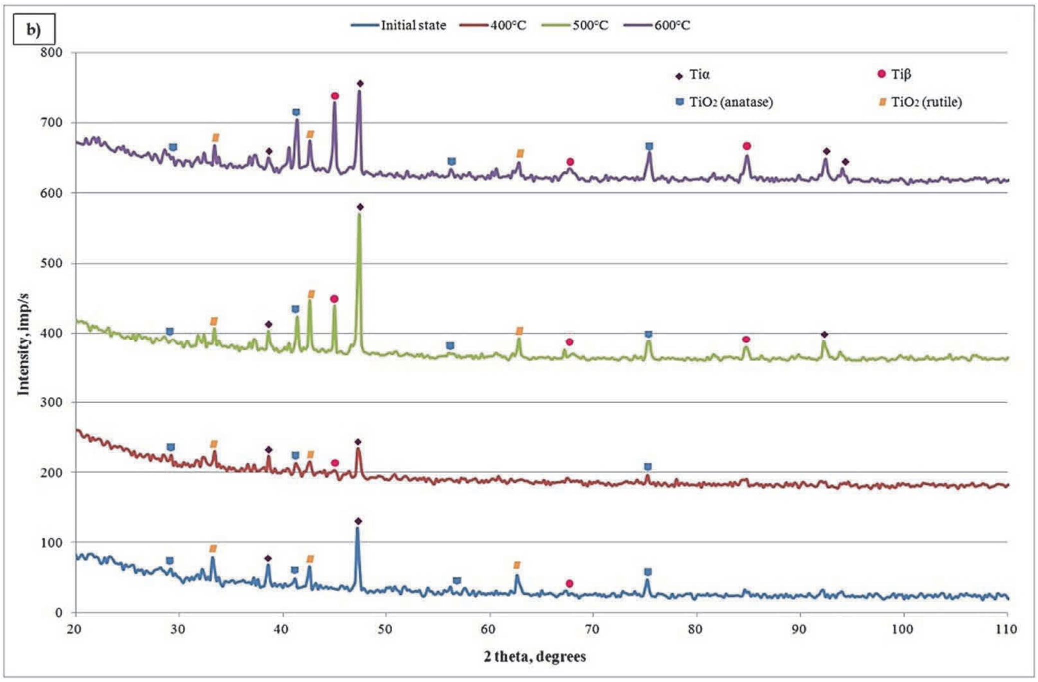



**Figure 4** Diffractograms of the titanium alloy after thermal oxidation at appropriate temperatures: a) 100% Ti-6Al-4V (bulk alloy), b) 100% Ti-6Al-4V (porous sinters)

## 4. CONCLUSIONS

The surface treatment used in the study led to the formation of a oxide layer $TiO_2$, which is characterized by high biocompatibility and non-toxicity for human tissues. Microstructure analysis and X-ray quality analysis confirmed presence of titanium phases: Tiα, Tiβ and oxide $TiO_2$ (anatase and rutile). The results obtained in the study showed that the increase in oxidation temperature causes an increase in the amount of oxides present on the surface.

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