

The comparison of oxide layers on selected bio-compatible titanium alloys

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Abstract

This paper discusses issues of growth of a thin oxide layer formed on the surface of titanium alloys. The oxide layer on the surface introduces a corrosion resistance and a bio-compatibility, both of which are required for medical applications. The oxide layer is a result of a spontaneous passivation, but for the practical applications it is necessary to control the growth of oxides. In present work, the oxide layer was formed on the CP Ti grade 2, Ti39Nb alloy and CP Ti grade 2 with Ti39Nb PVD coating of two different thicknesses by a thermal oxidation at 600 °C for 8 hours. After the oxidation process the surface roughness was measured, then the surface of samples and the cross-section of oxide layers were observed by SEM.

Keywords: titanium, oxide layer, TiNb, coating, biomaterials, EDS, surface roughness, thermal oxidation

1. Introduction

Nowadays, there is a need for better bio-implants and better bio-materials. It is due to several reasons: prolonging of human life, different lifestyle and activities, formerly incurable diseases and injuries. This may lead to the repairing or replacing parts of human body. The replacement should fit perfectly, act as the integral part of the body, have long lifetime, be bio-compatible, corrosion resistant and should not be expensive [1-3].

This work deals with creation, kinetic of growth and with properties of oxide layer formed on the thin coating from titanium alloy compared to the bulk materials. The work aims to be a starting point for further investigation. Because the problematic of thermal oxidation of materials with thin PVD coating was not fully researched. The results bring knowledge how to improve surface treatment of materials applied in bio-medicine.

1.1. Biomaterials

There are numerous existing materials used for body replacements. Predominantly used are titanium alloys (especially Ti-6Al-4V and CP titanium) and stainless steel AISI 316L [1].

The stainless austenitic steel AISI 316LVM is a material commonly used for orthopedic implants and is widely chosen because of its low price, easy production and less complicated welding in comparison to titanium, titanium alloys and alloys on Cr-Mo basis, while the properties for biomedical application are maintained [1].

Pure titanium, known as CP titanium (where CP stands for Commercially Pure), is another material widely used in many biomedical applications, e.g. cranial plates, maxillofacial reconstruction, dental implants, bone fracture fixations and prosthetic joints [2]. The most common among CP Ti materials are four grades, CP Ti grade 1 (99.5 wt. % Ti), grade 2 (99.3 wt. % Ti),

grade 3 (99.3 wt. % Ti) and grade 4 (99.0 wt. % Ti). Although each material contains slightly different levels of N, Fe, and O, C is specified <0.10 wt. % and H is also specified <0.015 wt. % [2,3].

Ti-6Al-4V alloy belongs to titanium $\alpha + \beta$ alloys and because of the combination of high resistance against corrosion, good chemical and mechanical properties it is one of the most used alloys in bio-medicine. Although some of the studies [3,4] indicate that there is a possibility of releasing ions of Al and V as a result of a long-term contact with the human body. These ions may cause the Alzheimer's disease or osteomalacia [2-6].

Due to the possible toxicity of Ti-6Al-4V alloys and further effort to improve the properties of bio-materials, new materials are being investigated. One of the ways to use Ti alloys without Al and V addition are the titanium β alloys, stabilized by Nb; they are achieving the suitability in mechanical properties as well in corrosion resistance and bio-compatibility [1,5-8].

1.2. Oxide layer

The corrosion resistance of titanium and its alloys is strongly influenced by a thin oxide layer which is forming itself on the surface of material. The forming of this layer is a result of high reactivity of titanium and the layer growth is initiated in micro-seconds after the exposure of Ti material to the atmosphere or moisture [2].

The growth rate of oxide layer may be increased by changing of external conditions – exposing the material to stronger oxidizing environment, e.g. heating on the higher temperatures, exposure to stronger oxidants (HNO₃, CrO₃ etc.), or anodic oxidation [9,10].

The resulting oxide layer is composed of three oxides: TiO₂, Ti₂O₃ and TiO. Among these, the titanium dioxide (TiO₂) is the most common and the most thermodynamically stable, it is the primary oxide from which the oxide layer on Ti and Ti alloys is consisted. TiO₂ oc-

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curs naturally in three modifications (anatase, brookite and rutile). The three modifications have the same chemical composition, they differ in the configuration of their atoms. This different structure is the reason for the different properties; the rutile phase is stable up to the melting temperature (as oppose to anatase and brookite which are unstable), and as the authors [2,11] note, is in some cases more suitable for the human body [2,10-13].

The layer is primarily formed by titanium oxides, but in the composition may appear more complex oxides (e.g. Al_2TiO_5 on Ti-6Al-4V, Nb_2O_5 and NbO_2 on TiNb, or NiTiO_3 on NiTi). In other cases the titanium oxides are doped with small amount of other elements (elements from the substrate material or the oxidation atmosphere). These small doses may then affect the properties of oxide layer (e.g. TiO_2 on TiNb alloys may be doped with small amount of Nb; this results in better bio-compatibility) [2,12,14].

2. Experiment

The experiment was based on the comparison of the oxidation results on CP Ti grade 2 and TiNb alloy with 39 wt.% of Nb (from now on Ti39Nb). Bulk samples and substrates for coating were prepared by grinding and polishing to mirror sheen. Afterwards, the two groups of CP Ti samples were coated by Ti39Nb (one with 2 μm , other with 5 μm of Ti39Nb) using Flexicoat 850, Hauzer. Subsequently, the samples were oxidized.

The type of oxidation process and its parameters were based on the literature [7,9,10]: oxidation at temperature of 600 °C in the air atmosphere at atmospheric pressure with dwell of 8 hours in the LAC LH 30/13 furnace equipped with MT825-A regulator. The course of the oxidation was following: heating from the room temperature with speed of 7.5 °C/min up to required 600 °C (see Fig. 1). At the end of the oxidation period, the furnace was turned off and the samples were cooled down to ambient temperature. It was expected that this process would result in formation of oxide layers with good adhesion to the substrate material.

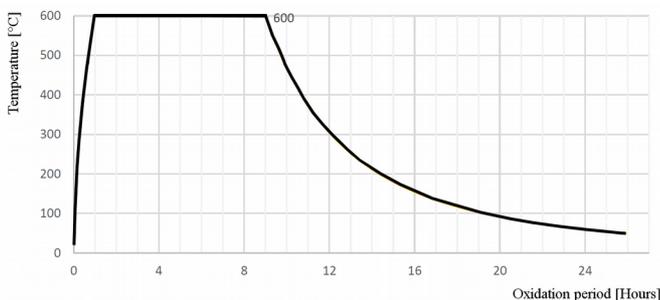


Fig. 1. Thermal oxidation process

Then the surface roughness was measured using-HOMMEL TESTER T100. The measurement of oxide layers was carried out on the surface and the cross-section of samples using the JEOL JSM 7600F scanning electron microscope.

3. Results and discussion

The results from the experiment will follow; firstly the measured and compared roughness of the samples, then the microscopic analysis of both the surface and cross-sections of samples.

3.1. Surface roughness

The growth of oxides on the surface of specimens leads to increase of the roughness of the surface: the roughness is increasing with the thickness of layer and the size of oxides. The change of surface roughness indicates the existence of oxide layer. In this work the objective was to measure the roughness of oxidized specimens and observe the changes of the surface roughness based on the substrate material. The surface roughness measurements were put in the chart (see Fig. 2). The results shown that oxidized specimens have higher surface roughness. Observed results agree with outcomes mentioned in [2,7].

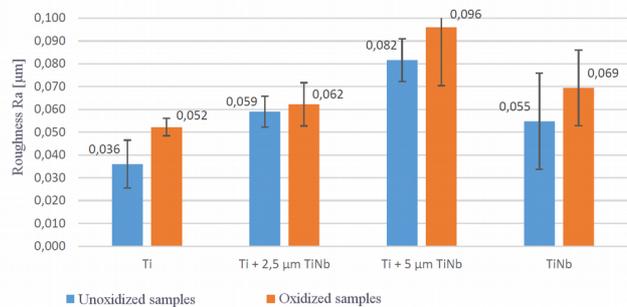


Fig. 2. Change of surface roughness

The change of surface roughness was similar on all groups of samples. The only exception being CP Ti with 2 μm of Ti39Nb, but this is more likely due to the higher roughness of the polished sample than due to the difference in oxide layer.

3.2. Microscopic analysis

The Figs. 3-6 represents the surfaces and the cross-sections of all 4 groups of oxidized samples. The substrate material, the coating and the oxide layer are labelled in every figure.

The Fig 1. shows oxidized sample of CP Ti grade 2. The surface was covered with oxide crystals (Fig. 1a)), especially on grain boundaries. The measured thickness of the oxide layer was app. 500 nm (Fig. 1b)). Samples from CP Ti with coating of Ti39Nb are in Fig. 2 and 3. For both of them was the surface uniformly covered with oxides (Figs. 2a) and 3a)). On the sample with 2 μm thick coating the oxide layer with thickness ranging from 300 nm to 400 nm was found (Fig. 2b)). The oxide layer thickness on the sample with 5 μm coating was ranging from 200 nm to 300 nm (Fig. 3b)). In the case of oxidized sample of Ti39Nb (Fig. 2), the oxide layer was considerably thinner than in case of the sample from CP Ti. In average, the thickness was app. 140 nm (Fig. 4b)).

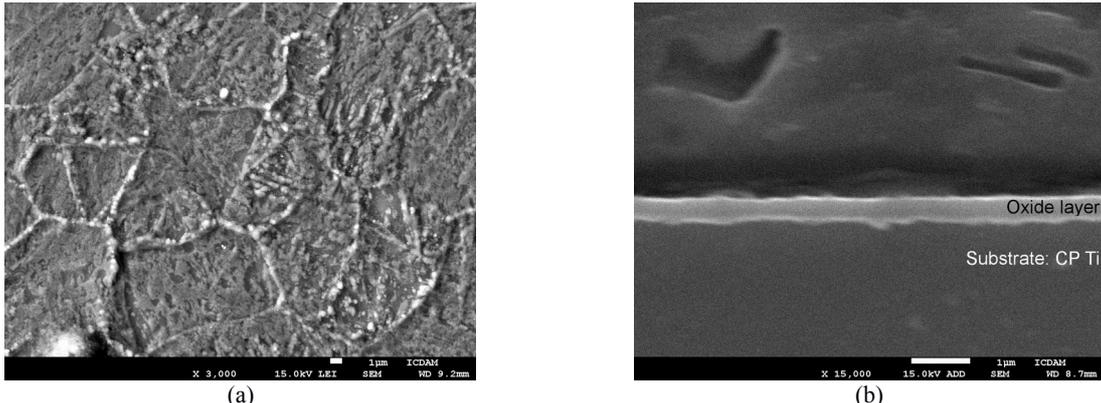


Fig. 3. Surface (a) and cross-section (b) of thermally oxidized CP Ti grade

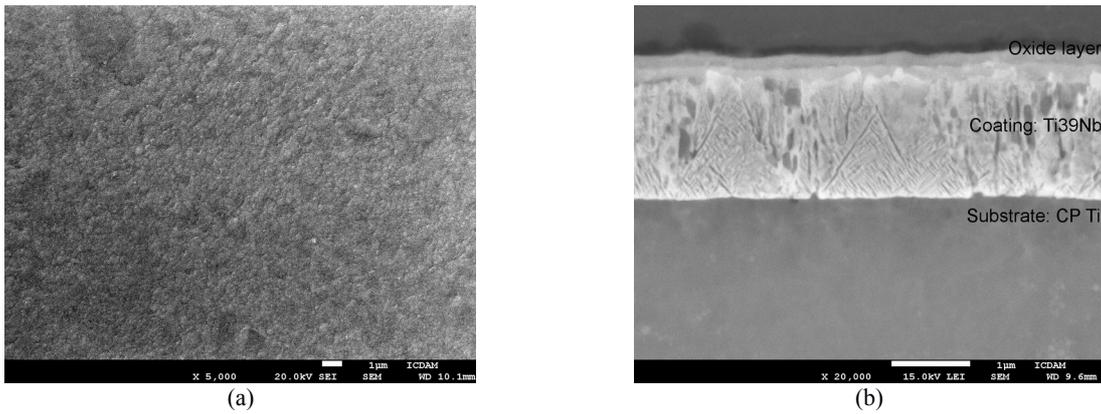


Fig. 4. Surface (a) and cross-section (b) of thermally oxidized CP Ti grade 2 with 2 µm of Ti39Nb

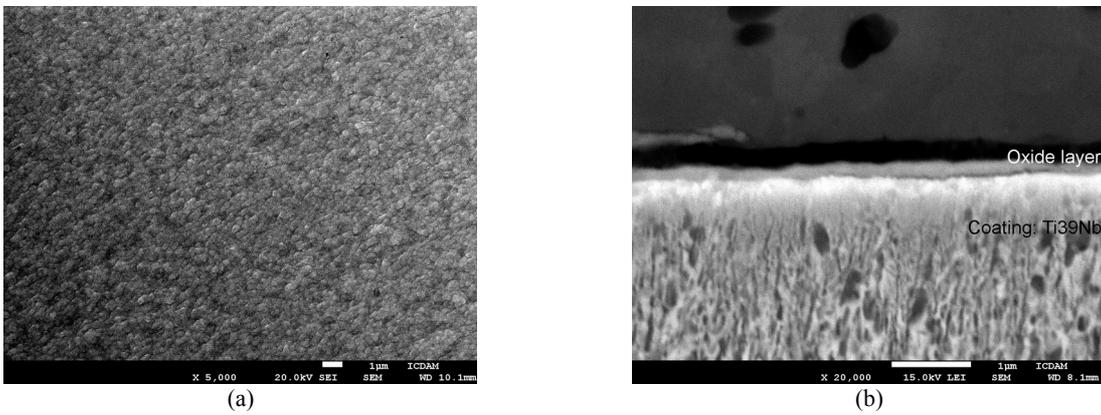


Fig. 5. Surface (a) and cross-section (b) of thermally oxidized CP Ti grade 2 with 5 µm of Ti39Nb

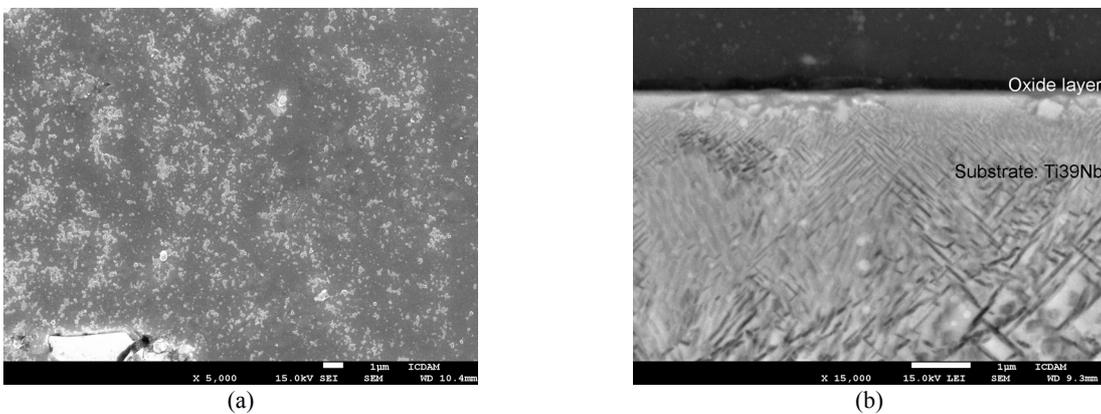


Fig. 6. Surface (a) and cross-section (b) of thermally oxidized Ti39Nb

From the images it is evident that the oxide layers formed on all samples are compact and with relatively uniform thickness. The adhesion of the oxide layers to the substrate/coating seems to be the same for all samples. The main difference between oxide layers was found in the resulting thickness. The thickest layer was found on CP Ti grade 2, the thinnest one on Ti39Nb. The thickness of oxide layers on Ti39Nb coatings was in between.

These preliminary results indicate that the TiNb alloy appears to be less vulnerable to the oxidation process than CP Ti grade 2 or that passivation process on TiNb alloy is stronger than on CP Ti grade 2. It leads to the formation of thinner oxide layer when compared to the samples of CP Ti grade 2 which were oxidized in the same conditions and in the very same process. These findings contradict to the information found in the literature [6]. This phenomenon should be further investigated using different oxidizing conditions when compared with other materials and with other methods of the oxidation process.

3.3. Chemical analysis

On the specimen where the oxide layer was the best contrast (2 of Ti39Nb) the EDS analysis was performed (see Fig. 7). It is a line EDS analysis allowing an approximate identification of elements. The violet line stands for oxygen, red for titanium, green for niobium, violet for aluminium from the foil (more detailed results see on the Fig. 8). Oxygen signalizes the oxide layer. Ti and Nb are present in the oxide layer as well as in the PVD coating. Ti is in results present due substrate material.

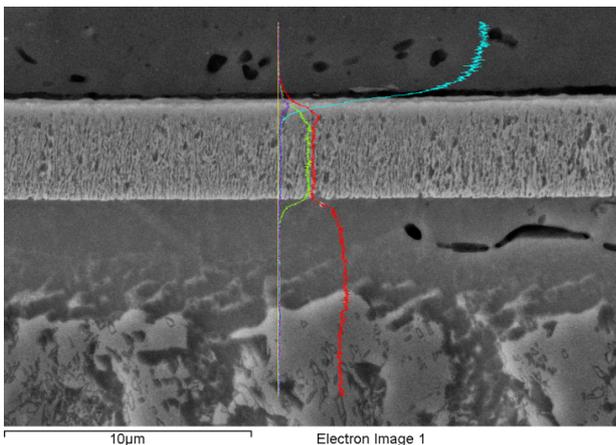


Fig. 7. EDS Chemical analysis on cross-section of CP Ti with 2 μm of TiNb

It can be seen, that in the substrate material Ti prevails, whereas Ti and Nb form the majority in the coating and oxygen prevails in the surface layer. As it has been mentioned above, these results are not exact and serve only as the approximate verification of the oxide presence in the newly formed layers. In case of any other experiments it will be more appropriate to use other methods of EDS analysis and X-ray diffraction to analysis the phases of the oxides. These methods will not only

provide more exact data, but it will be possible to distinguish and define various oxides and their structures.

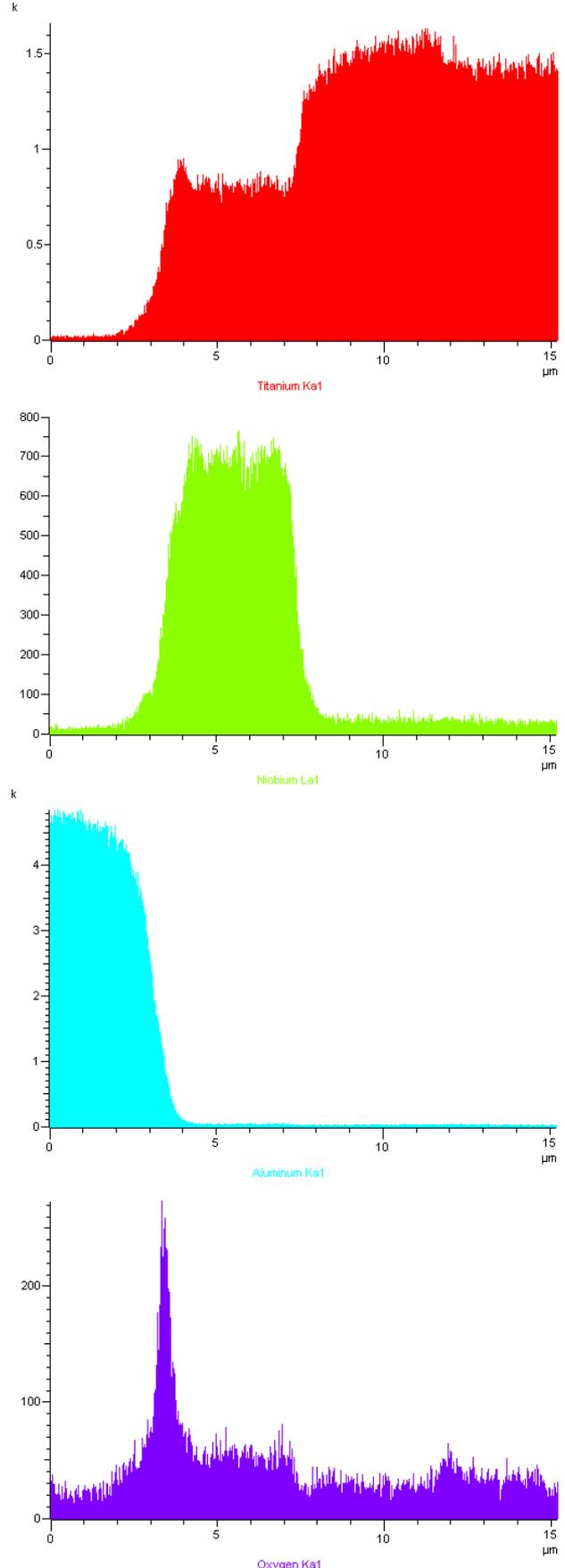


Fig. 8. Results of EDS Chemical analysis on cross-section of CP Ti with 2 μm of TiNb

4. Conclusions

- The oxide layer was created by the thermal oxidation on all four groups of samples and resulted in oxide layers of different thickness. This has been proven by the EDS line analysis.
- The surface roughness of polished and oxidized samples was measured and compared. The change of surface roughness was similar on all four groups of samples. Hence the influence of material and its chemical composition is in this case minimal.
- However against the assumption, the thickness of the oxide layers showed a different trend than the one noted in literature.
- The oxide layer found on the samples with thicker Ti39Nb coating was thinner than on the samples with thinner Ti39Nb coating.
- The results indicate the dependence between the thickness of Ti39Nb coating and the thickness of the resulting oxide layer.
- It will be further investigated how the results will differ under different oxidation conditions and with use of others method of oxidation.

Acknowledgments

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