



PROPERTIES AND STRUCTURE OF OXIDE LAYERS ON A THIN COATING OF A TITANIUM-NIOBIUM ALLOY

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Resume

Present work discusses issues of growth and characterization of a thin oxide layer formed on the surface of a titanium-niobium alloy. An oxide layer on the surface of titanium alloys introduces a corrosion resistance and also a bio-compatibility, which is required for a medical application. Although this oxide layer is a result of a spontaneous passivation, for the practical applications it is necessary to control the growth of oxides. In this work the oxide layer was formed on the PVD coating from Ti39Nb alloy which was sputtered on three different base materials: CP Ti grade 2, stainless steel AISI 316LVM and titanium alloy Ti-6Al-4V ELI. The oxide layer was created by a thermal oxidation at 600 °C for three different oxidation periods: 1, 4 and 8 hours. After the oxidation process the influence of oxidation characteristics and base materials on the thickness and properties of oxide layer was studied. There was observed a change of color and surface roughness. The oxide layer surface as well as the layer thickness was observed by SEM. The influence of the substrate material under the coating on the oxide layer should be more investigated in the future.

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1. Introduction

The need for better bio-materials used for medical application (implants and surgical tools) grows significantly with prolonging of active human life and with the increase of physical activity. This leads to ways of research heading towards finding new materials, or improving old materials, which would perform better in the areas of bio-compatibility (or bio-activity), mechanical properties, corrosion resistance and others. The aim is to find a material which would intergrade as a natural part of body, would be able to bear stress and which would be economically beneficial. One of the possible ways of development is the usage of coating from highly bio-compatible material on the base material from material with acceptable mechanical properties [1, 2].

This work deals with creation, kinetic of growth and with properties of oxide layer formed on the thin coating from titanium alloy. 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

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, 3, 5, 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. The titanium β alloys, stabilized by Nb, are one of the possibilities; they are achieving the suitability in mechanical properties as in corrosion resistance and bio-compatibility [1, 5 – 8].

1.2 Oxide layer

The corrosion resistance of titanium and its alloys is caused 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 just 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 (HNO_3 , CrO_3 etc.), or anodic oxidation [9, 10].

The resulting oxide layer is composed of three oxides: TiO_2 , Ti_2O_3 and TiO . Among these, the titanium dioxide (TiO_2) 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. TiO_2 occurs in nature in three modifications (anatase, brookite and rutile); it is possible to obtain other modifications synthetically and due to high pressure. 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 in every temperature (as oppose to anatase and brookite which are unstable), and as the author [2] notes, is the most suitable for the human body [2, 11-13].

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 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

Three specimens of CP Ti grade-2, Ti-6Al-4V ELI alloy and stainless steel AISI 316LVM in the form of cylindrical bars, were used in this study (see Table 1 for chemical composition of materials).

The bars were cut into the specimens with diameter 15 mm and thickness 8 mm. Flat planes of specimens were ground and polished to obtain a surface with a mirror look. The PVD coating was then created on the polished specimen surfaces (see Table 2 for PVD coating parameters) in the Flexicoat 850, Hauzer. For the coating was used target made of alloy Ti39Nb.

Specimens with PVD coating were subject to thermal oxidation.

2.1 Experiment characterization

The parameters of the oxidation were chosen according to the literature [2, 7, 8, 15]. The sample was subjected to the oxidation at 600 °C in a furnace LAC LH 30/13 with regulator MT825-A at the presence of air on atmospheric pressure for 3 distinct periods: 1, 4 and 8 hours.

The furnace heating started at room temperature and continued gradually with speed of 7.5 °C/min up to 600 °C. After the oxidation period elapsed, the heating was switched off and the specimens were left to cool down to the room temperature. For the details about the oxidation process (speed of heating and cooling) see Fig. 1. This form of oxidation process was expected to provide oxide layers with good adhesion to substrate material.

Table 1

Chemical compositions of CP Ti grade 2, stainless steel AISI 316LVM and Ti-6Al-4V ELI.

Chemical composition of CP Ti grade 2 (wt. %) (maximal amounts)										
O	N	C	H	Fe	Al	V	Ni	Mo	others	Ti
0.25	0.0300	0.0800	0.0125	0.3000	---	---	---	---	---	balance
Chemical composition of stainless steel AISI 316LVM (wt. %) (maximal amounts)										
C	Si	Mn	P	S	Cr	Mo	Ni	Cu	N	PRE
0.0220	0.3500	1.7500	0.0210	0.0010	17.1800	2.7100	14.1000	0.0600	0.0940	26.1230
Chemical composition of alloy Ti-6Al-4V ELI (wt. %) (maximal amounts)										
O	N	C	H	Fe	Al	V	Ni	Mo	others	Ti
0.1300	0.0500	0.0800	0.0120	0.2500	6.5000	4.5000	---	---	---	balance

Table 2

The parameters of PVD coating.

Parameter	Temperature (°C)	Current (A)	Sputtering power (kW)	Pressure (Pa)	Thickness (µm)
Value	250	5	4	200	1.0-1.5

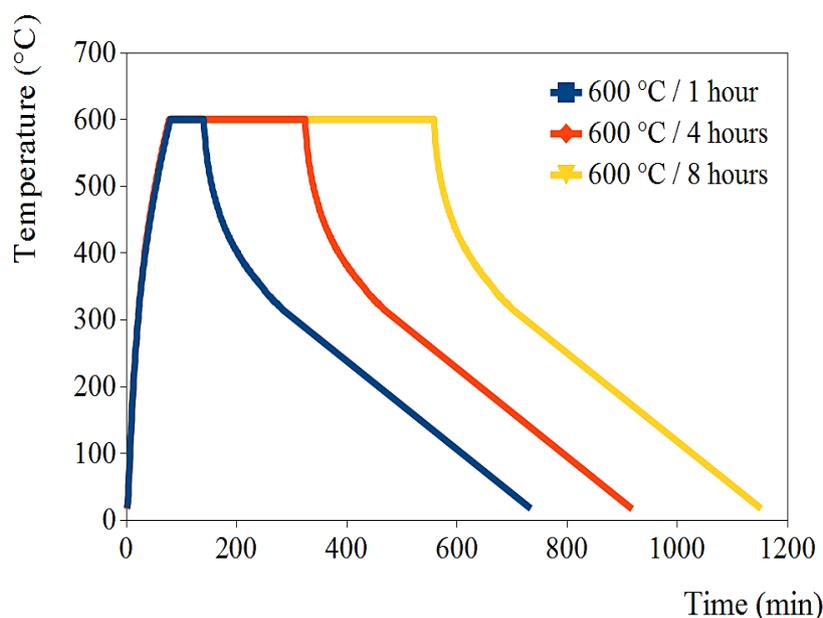


Fig. 1. Thermal oxidation process.
(full colour version available online)

After the removal of specimens from the furnace was on their surface observed a change of color and the roughness of surfaces was measured. Then the surface of the specimens was observed and the thickness of the oxide layer was measured by the scanning electron microscope JEOL JSM 7600F equipped with an energy-dispersive X-ray analysis system (EDS).

3. Results and discussion

3.1 Surface color

The observation of the surfaces of oxidized specimens has shown the change of color. It can be seen that the color is changing with the increase of the oxidation period.

For the shorter periods of time, the color was dark blue. For the specimens from AISI 316LVM with TiNb coating (see Fig. 2) can be seen that the color changes into the purple with gold accent (4 hours) and silver accent (8 hours) with longer oxidation. For the titanium based substrate materials with Ti39Nb coating (see Fig. 3 and 4) the blue color changed into light blue/green with silver accent.

All these observation of the surface colors coincides with observations described in [2]. The change of color indicates the creation of oxide layer, and further change of color with prolonging oxidation period indicates change in the thickness of oxide layer.

3.2 Surface roughness

As it is described in literature [2], 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, as well as the change of surface color, 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 (a) the oxidation conditions and on (b) the substrate material. The surface roughness measurement is summarized in Table 3. The results shown that oxidized specimens have higher surface roughness which increases with longer oxidation period. Observed results agree with outcomes mentioned in [2].

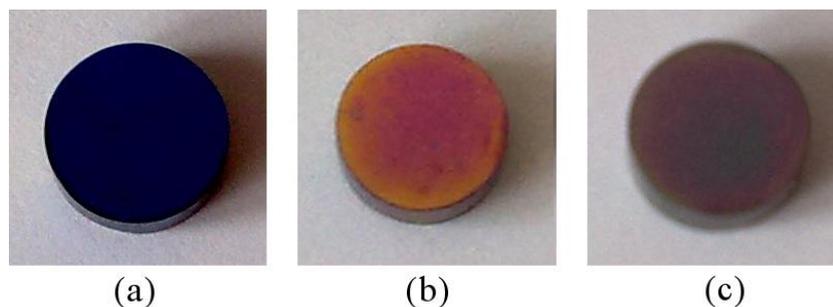


Fig. 2. Surface color on 316LVM+Ti39Nb; oxidation 600 °C; a) 1 hour; b) 4 hours; c) 8 hours. (full colour version available online)

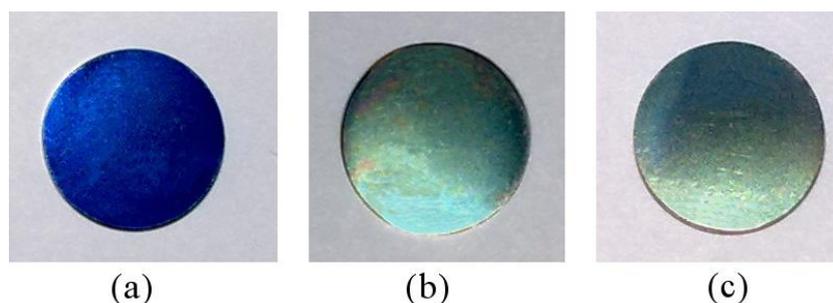


Fig. 3. Surface color on Ti grade-2+Ti39Nb; oxidation 600 °C; a) 1 hour; b) 4 hours; c) 8 hours. (full colour version available online)

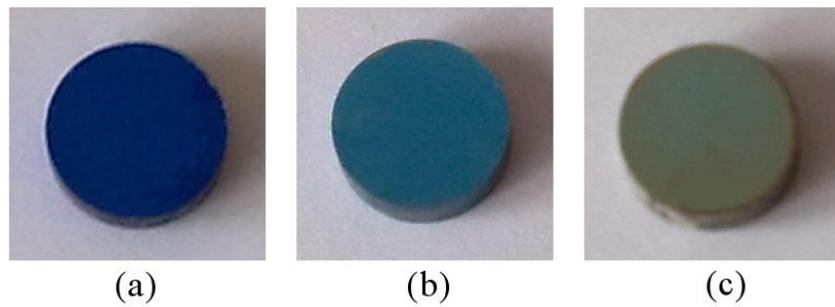


Fig. 4. Surface color on Ti–6Al–4V ELI+Ti39Nb; oxidation 600 °C; a) 1 hour; b) 4 hours; c) 8 hours. (full colour version available online)

Table 3

Surface roughness of specimens; Ti g 2, 316LVM and Ti–6Al–4V ELI with Ti39Nb coatings.

Test condition	Ra (µm) (average value)		
	CP Ti grade 2	Steel AISI 316LVM	Ti–6Al–4V ELI
Not-oxidized	0.030	0.010	0.020
Oxidized: 600 °C, 1 hour	0.051	0.020	0.060
Oxidized: 600 °C, 4 hours	0.060	0.026	0.074
Oxidized: 600 °C, 8 hours	0.086	0.053	0.083

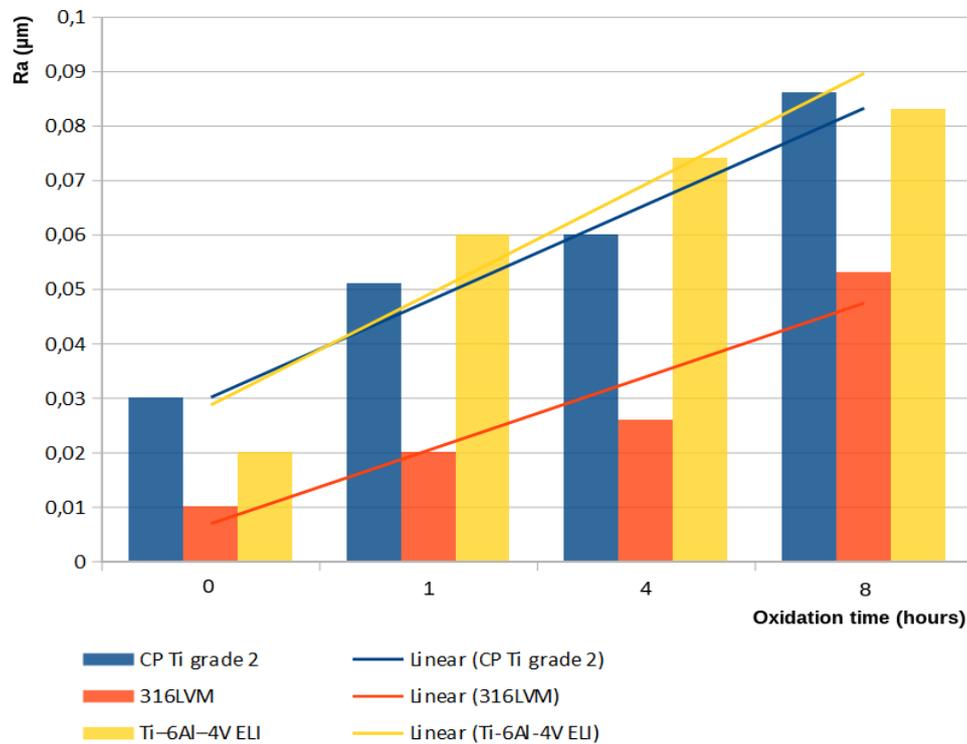


Fig. 5. Change of surface roughness with prolonging oxidation period; CP Ti grade 2, 316LVM and Ti–6Al–4V ELI with Ti39Nb coatings. (full colour version available online)

The results were put into a chart (see Fig. 5) to visualize the evolution of surface roughness with increasing oxidation time.

The growth of roughness was observed for all the substrate materials with Ti39Nb coating. After the 8-hour oxidation the surface roughness was

approximately three times higher than on the untreated specimens for all substrate materials. To compare the materials, we have calculated a linear regression of each substrate. It can be seen that the increase rate is roughly the same for all substrate materials with Ti39Nb coating. The only difference is due to the initial states of the specimen surfaces. Even though all of specimens were prepared in the same manner, difference was predetermined by the substrate materials themselves.

3.3 Surface structure and layer thickness

The surface of specimens with a substrate material 316LVM (see the left micrograph in the Fig. 6) indicates a presence of crystal oxides (marked in Fig. 6a) even after a short oxidation period. The size and mount of oxides rapidly increases with the oxidation period. This coincides with the measurement of oxide layer thickness (right micrograph in Fig. 6). In consent with growth of crystals was detected measurable oxide layer (see the right side of Fig. 6).

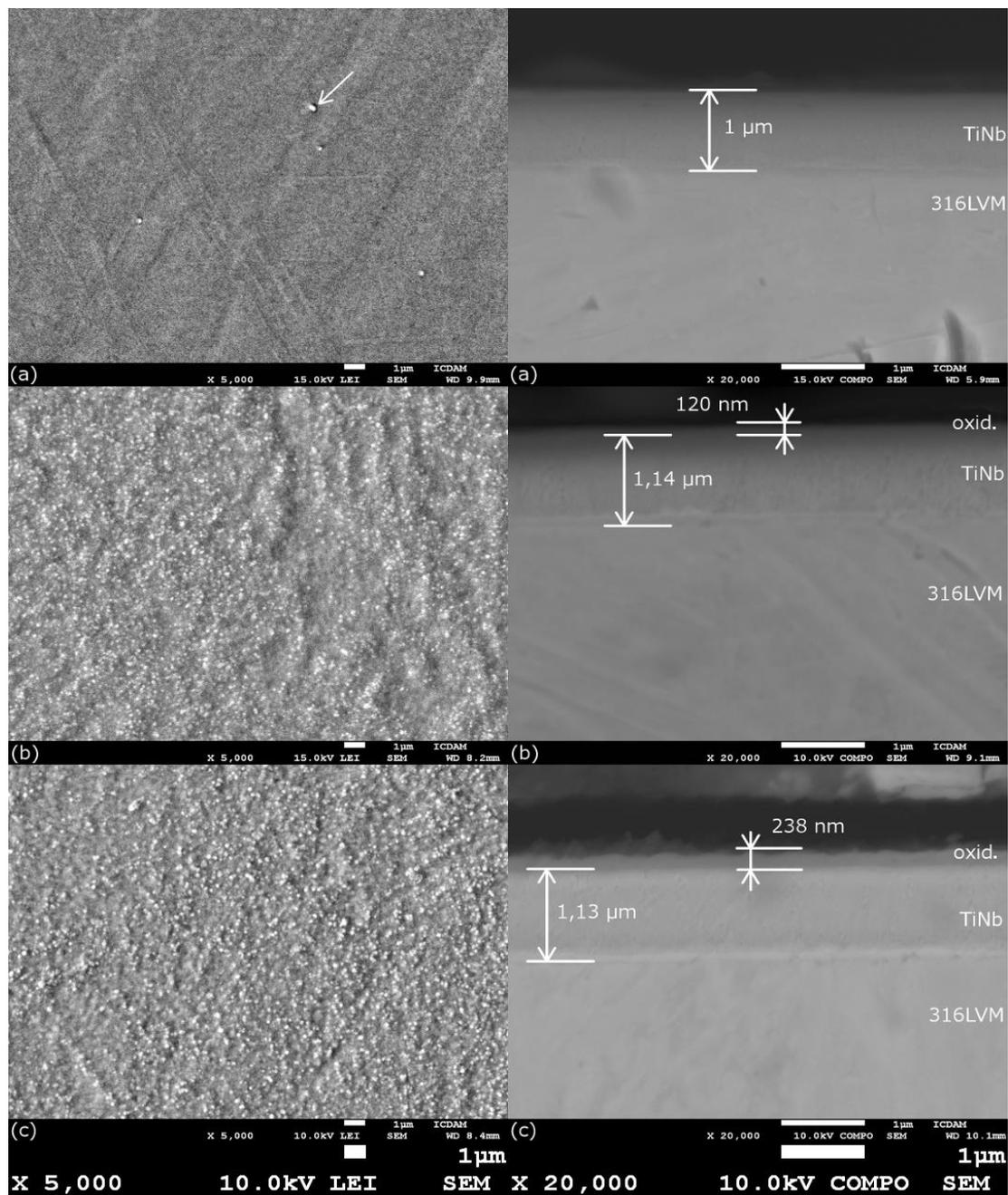


Fig. 6. SEM micrograph of specimen surface and cross-section detail view of specimen with oxide layer; 316LVM+Ti39Nb; oxid. at 600 °C, for a) 1; b) 4; c) 8 hours.

In the case of 4-hour oxidation (Fig. 6b) was observed a 120 nm thick oxide layer with worse contrast. After the 8-hour oxidation (Fig. 6c) a clearly visible 240 nm layer was detected.

The surface of specimens with substrate material CP Ti grade 2 (see the left micrograph in Fig. 7) exposed to a short-term oxidation indicates a presence of crystal oxides (marked in Fig. 7a). With longer oxidation period

the size and amount of crystals increased but not as much as in the previous case. The measurable oxide layer was also detected (see the right side micrograph in Fig. 7). In the case of 4-hour oxidation (see Fig. 7b) the oxide layer was rather thin (54 nm) and poorly distinguishable. After the 8-hour oxidation (see Fig. 7c) was detected a compact and strong oxide layer (290 nm). However, its contrast is lower than in the case of specimens from 316LVM.

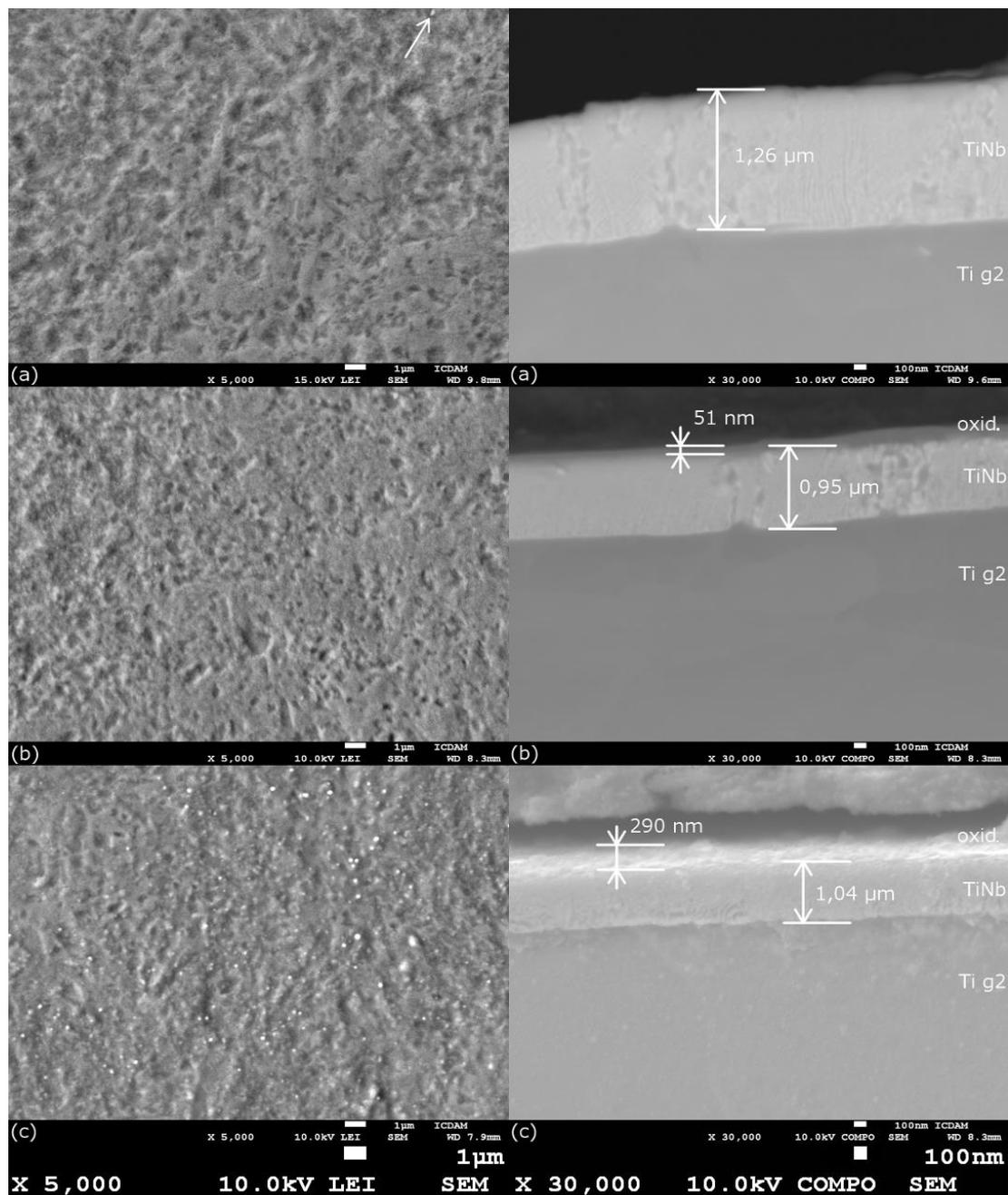


Fig. 7. SEM micrograph of specimen surface and cross-section detail view of specimen with oxide layer; CP Ti grade 2+Ti39Nb; oxid. at 600 °C, for a) 1; b) 4; c) 8 hours.

We have found just a small amount of oxide crystals on the surface of specimens with substrate material Ti-6Al-4V ELI (see the left micrograph in Fig. 8). The amount and the size of crystals was increasing with oxidation period length but not as much as it was observed on previous two groups of specimens. We also have not detected any measurable oxide layer on any of these specimens (see the right micrograph in Fig.8).

of surface and the measurements of the coating and oxide layer showed that there is a visible relationship. The growth of oxides (i.e. both the size as well as the amount of the oxide particles) on the surface of coating indicated (as well as the change of the color and roughness) the increase of thickness of the oxide layer. Measurements of the size, the amount and the placement of oxides on the specimen surface were not realized. It remains as an objective for later works.

A comparison of the micrographs

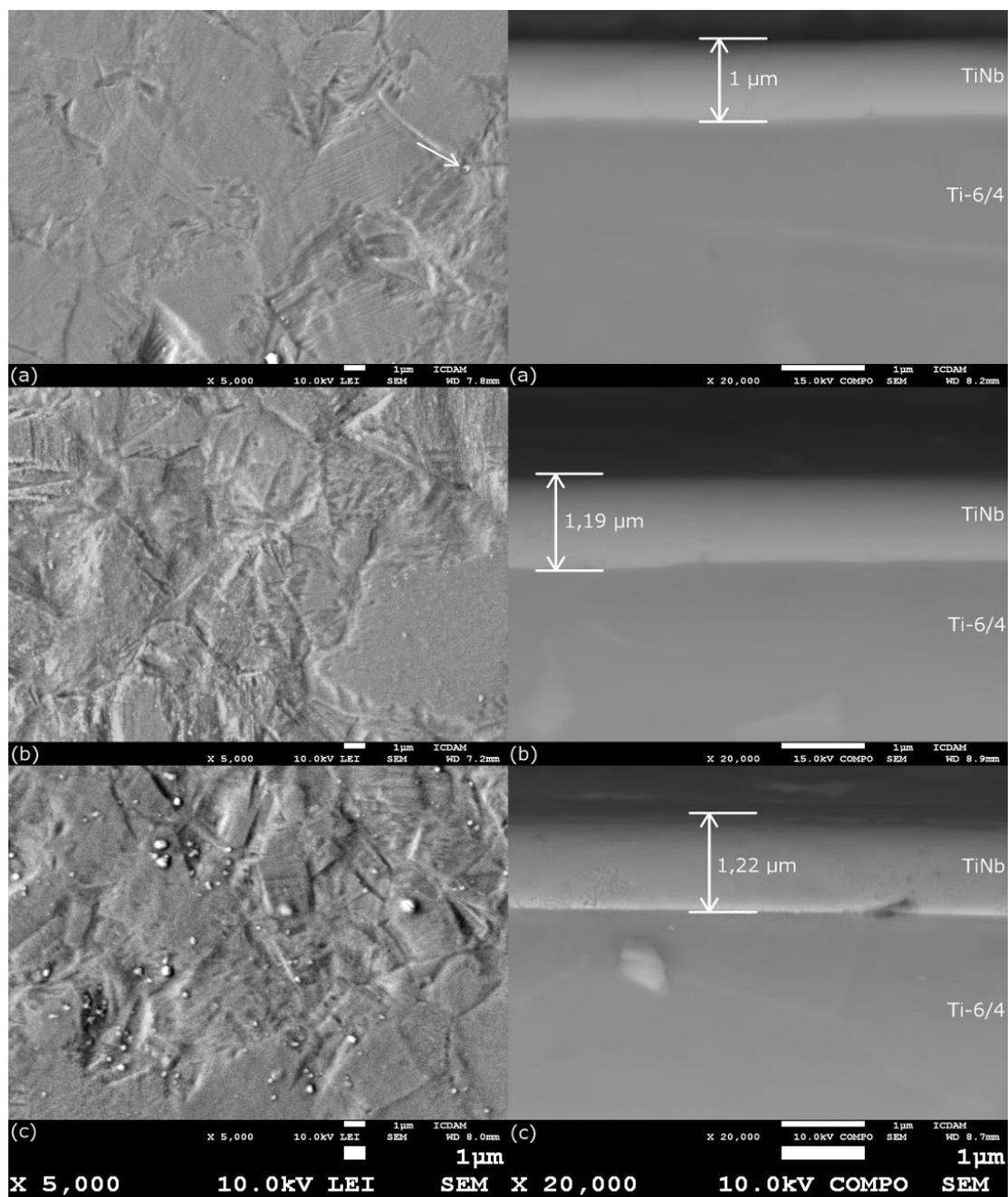


Fig. 8. SEM micrograph of specimen surface and cross-section detail view of specimen; Ti-6Al-4V ELI+Ti39Nb; oxid. at 600 °C, for a) 1; b) 4; c) 8 hours.

It was observed that the oxide layer does not depend only on the coating; the growth of the oxides was also affected by the substrate material. The best results were obtained on the specimens with the substrate material from stainless steel 316LVM. The oxide layer is compact, well visible and measurable as well as the oxide crystals on the surface. However, we have not observed any measurable oxide layer on the surface of specimens with substrate material from Ti-6Al-4V ELI only isolated crystals are present on the surface (though their size exceeds that of all other specimens). The influence of the substrate material under the coating on the oxide layer should be more investigated in the future.

On the specimen where the oxide layer was the best contrast (316LVM with Ti39Nb coating oxidized for 8 hours) the EDS analysis was performed (see Fig. 9). It is a line EDS analysis allowing an approximate identification of elements. The blue line stands for oxygen, red for titanium, yellow for niobium, turquoise for

iron and others are backing elements (more detailed results see on the Fig. 10). Oxygen signalizes the oxide layer. Ti and Nb are present in the oxide layer as well as in the PVD coating. Fe, Cr and Ni are in results present due substrate material. The higher amount of silicon is in results present due to the preparation of the specimen (silica gel was used during polishing).

It can be seen, that in the substrate material Fe 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.

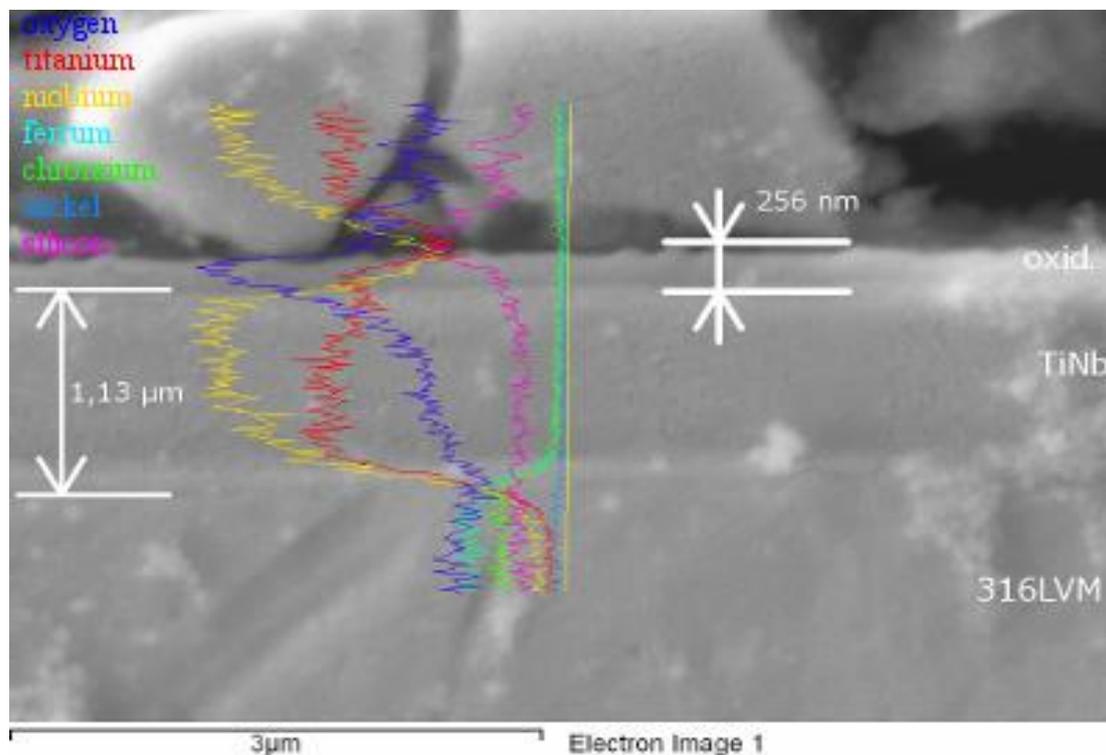


Fig. 9. SEM EDS line scan results of cross-section of the studied specimen 316LVM with Ti39Nb coating, oxidation: at 600 °C, for 8 hours. (full colour version available online)

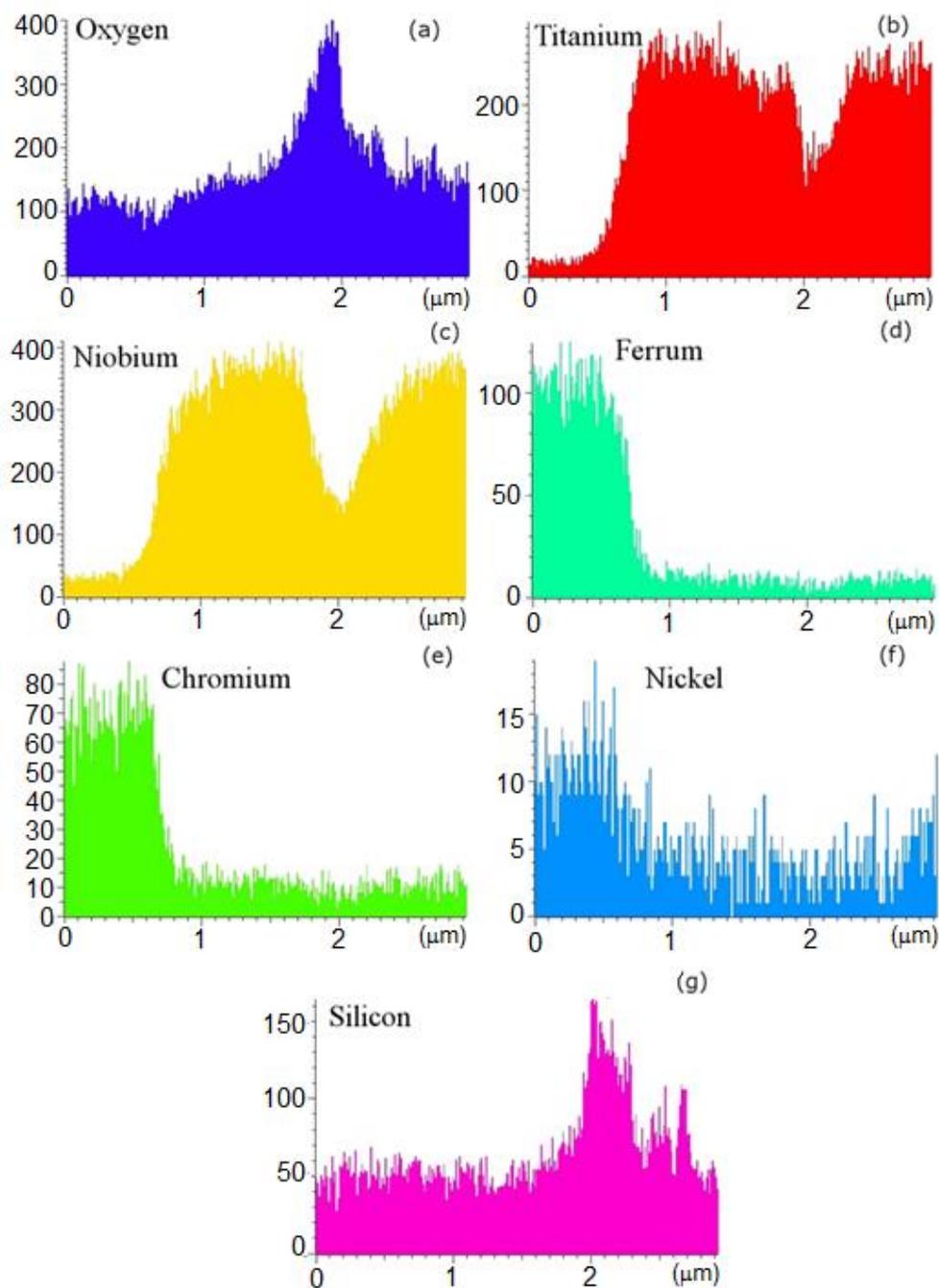


Fig. 10. SEM EDS line scan results of cross-section of the studied specimen 316LVM with Ti39Nb coating, oxidation: at 600 °C, for 8 hours; a) Oxygen; b) Titanium; c) Niobium; d) Ferrum; e) Chromium; f) Nickel; g) Silicon.

(full colour version available online)

4. Conclusions

- A thermal oxidation was preceded on a thin coating consisting of an alloy Ti39Nb which was sputtered on the surface of CP Ti grade 2, stainless steel AISI 316LVM and alloy Ti-6Al-4V ELI.
- A change of color was observed on the surfaces of oxidized specimens. This indicated a formation and existence of oxide layer of variable thickness.
- All of the oxidized specimens were showing the influence of oxidizing conditions on the surface roughness.

- Different growth rates of surface oxides throughout the oxidation period, depending upon the substrate material, were noted.
- There is no measurable oxide layer on the coating from alloy Ti39Nb on the specimens from the alloy Ti-6Al-4V ELI.
- In the case of specimens from CP Ti grade 2 and stainless steel AISI 316LVM were measured an oxide layer of variable thickness on the coating from alloy Ti39Nb, after the oxidation period of 4 and 8 hours.
- The thickest oxide layer was noted on the specimen with the substrate material CP Ti grade 2 with a coating from alloy Ti39Nb, after the oxidation during 600 °C and for the period of 8 hours.
- The relationship between growth of the oxides on the surface and the measured thickness of oxide layer was noted.
- In the next study, the characterization and the analysis of the oxide layers and their structure is considered to be done. The idea is to use the X-ray diffraction to identify the compounds and structured in the oxide layer.

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Note

Shorter and less complex version of this article was presented at the 25th Heat Treatment Days conference in Jihlava.

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