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Hybrid Oxidation of Titanium Substrates for Biomedical Applications

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Abstract: Titanium oxidation for biomedical applications is still a challenge in obtaining favorable mechanical and physicochemical properties of thin oxide layers as well as the required high bioactivity. Interesting techniques for TiO_2 layers formation are electrochemical, plasma and diffusive methods. Each method aims to create a thin oxide layer characterized by thermal stability and re-passivation in the presence of SBF environment. However, an important aspect here is also phase composition of oxide layers, essential for the osseointegration. Accordingly, research carried out aims to produce such a titanium substrate, where surface zone is $Ti_{\alpha}(O)$ solid solution formed with Fluidized Bed (FB) diffusion process (640 °C, 8 h) and the top layer is TiO_2 produced by PVD magnetron sputtering. Effects of such hybrid oxidation on titanium surface properties were investigated with SEM / STEM / RS and Nanoindentation tests. Results showed that hybrid oxidation made it possible to generate favorable synergetic effect between FB and PVD oxide layers and to reduce the stresses at their interface. In turn, variable share of TiO_2 phases (rutile + anatase mixture) obtained at the titanium surface allowed for the significant enhancement of hydroxyapatite compounds growth which was confirmed by 14 days Kokubo test.

Keywords: titanium oxidation; PVD magnetron sputtering; thin TiO_2 layer; bioactivity

1. Introduction

Titanium oxide thin layers are still the subject of numerous studies due to their highly interesting properties for biomedicine and implantology, especially for the third-generation biomaterials, which are produced to stimulate specific cell response and tissue regeneration [1–3]. In fact thin TiO_2 oxide layers obtained with the use of the several methods as: anodizing, laser treatment PLD, physical methods PVD and diffusion methods, have small thickness and not always good adhesion, which depends on many factors, including surface preparation for the oxidation, phase composition of surface oxides and substrates chemical and strength properties [4–7]. Nevertheless, each method aims to create a passive oxide coating, which is characterized by homogeneity, low thermal conductivity, chemical stability and the ability to re-passivate after being defected in the presence of corrosive environment. The mechanism of titanium oxidation differs from the oxidation of other metals. This is due to stability of the material: Ti_{α} – stable up to and Ti_{β} – stable over 882 °C. At room temperature on the Ti surface thin (5-15 nm) passive nanolayer is formed, where in turn oxidation of titanium at high temperature (> 400 °C), leads to formation of the crystalline layer with TiO/ inter Ti_2O_3 layer and TiO_2 layer (rutile or anatase) zone structure. The oxide coating formed at room temperature is stable and adheres well to the substrate, but is too thin. In turn, at high temperatures titanium oxidizes rapidly and forms thick oxide layer which is often porous, poorly bonded (anchored) to the substrate, and thus delaminates and cracks [8–11]. An important role of the oxide layer on the titanium surface in addition to the aforementioned properties is also to provide the required osseointegration process kinetics by forcing the biochemical activity of the layers leading to accelerated interaction with the body's tissues [12–16]. Initially, it was thought that the titanium substrates are inert to the body. However, in direct contact with tissues of organisms, titanium can release Ti ions into the body's environment, which causes the occurrence of edema and inflammation, generates health problems of patients and ultimately rejection of the implant. Biocompatibility and bioactivtiy of the titanium is directly related to the physicochemical properties of the substrate surface. To improve the bioactivity of titanium substrates most-known solutions are single-stage surface treatment, and production of multilayers [17–20]. However, surface methods due to the conditions of rapid chemical interaction between the atmosphere and substrate, have very limited influence on oxygen diffusion processes towards the substrates surface layer and formation of $Ti_\alpha(O)$ diffusion layer with good strength properties. Thus, it is difficult to obtain substrates with the following arrangement: I. Ti_α substrate / II. $Ti_\alpha(O)$ solid solution / III. thin TiO_2 oxide layer, having both stable oxide phases at the surface, low hardness gradient between matrix and layer and reduced state of stress (compressive stresses required) at the interface [21–24]. Accordingly, highly bioactive titanium materials (i.e., third generation metallic biomaterials) might be produced by adequate functionalization of the thin oxide layers (tailored phase composition morphology and adhesion to the substrate) together with controlling of substrate surface stress state and structure. Therefore, the research carried out by Author aims to develop such a titanium substrate, where on diffusion oxide layer ($Ti_\alpha(O)$ solid solution), homogenous, tight and smooth thin TiO_2 layer is being formed by surface treatment i.e., PVD magnetron sputtering. Such hybrid method uses the advantages of continuous substrate activation and defect by influence of a fluidized bed aeromechanical factor, and non-equilibrium PVD surface oxidation. There is expectation that combination of TiO_2 layers will ensure a synergistic effect on improving titanium substrates biofunctional properties.

2. Materials and Methods

The substrates used for hybrid oxidation were made of Ti_α single phase commercially pure titanium manufactured by Kobe Steel LTD in accordance to ASTM 8348, with chemical composition presented in Table 1.

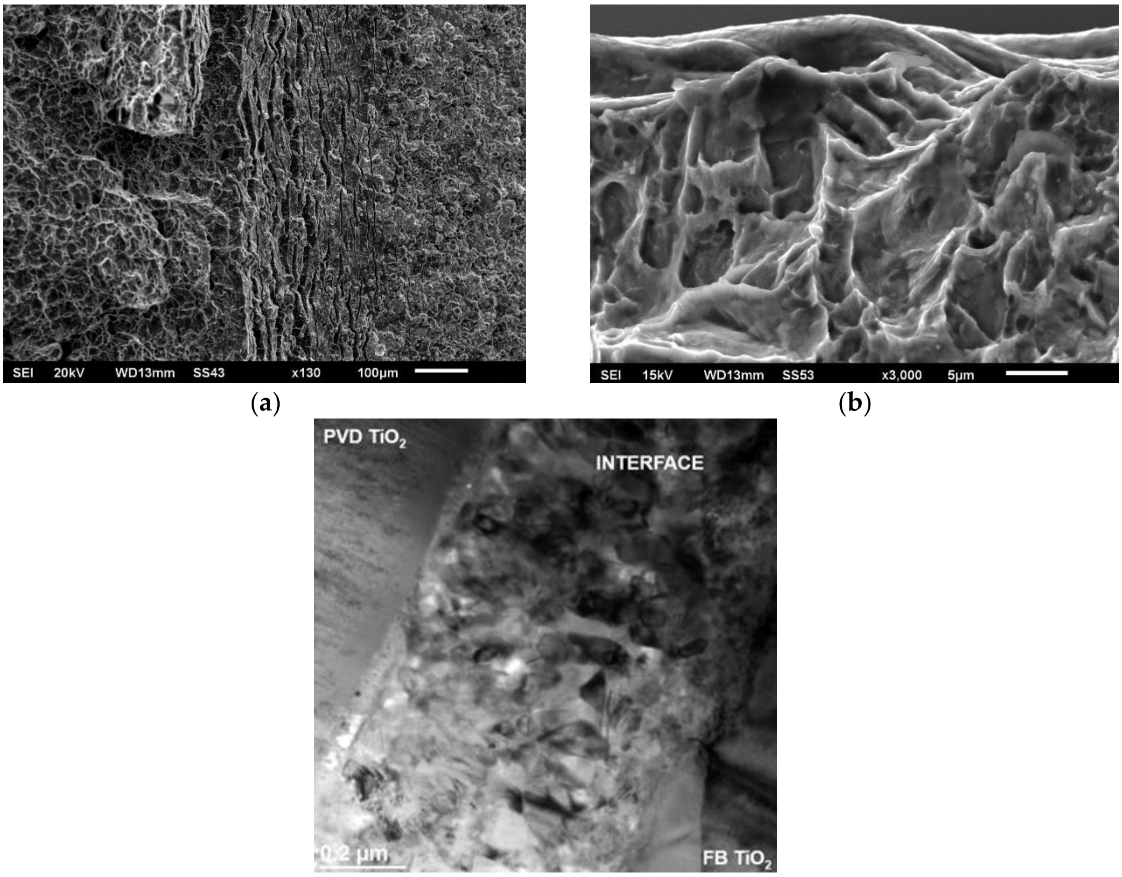
Table 1. The chemical composition of commercially pure titanium used for hybrid oxidation (in accordance with ASTM 8348), [mass %].

Material	Chemical Composition					
KOBE Steel LTD	O	N	C	H	Fe	Ti
Titanium Grade 2 (ASTM 8348)	0.20	0.03	0.10	0.015	0.30	rest

Before hybrid oxidation, substrates were mechanically activated by blasting with a mixture of Al_2O_3+ZrO_2+Ti. Diffusive oxidation was carried out in a fluidized bed (FB) reactor with Al_2O_3 grain material at 640 °C for 8 h in air atmosphere. After the FB treatment, substrates were cooled down in air. Further oxidation process was conducted with PVD magnetron sputtering using a TiO_2 target, pressure of 3×10^{-2} mbar, Ar (99.95%) atmosphere, constant power mode P = 350 W, target – substrate distance 60 mm and deposition time 20 min. Thin TiO_2 oxide layers structure and interface were analyzed by scanning electron microscopy SEM (FEI E-SEM XL30 microscope) and scanning transmission electron microscopy STEM (FEI S/TEM TITAN 80-300) method. Surface morphology of the substrates was evaluated by confocal laser scanning microscopy CLSM (OLYMPUS LEXT 4000 microscope). Phase analysis of TiO_2 layers was conducted by Raman Spectroscopy RS (Horriba Jobin Yvon LabRAM HR micro-Raman spectrometer equipped with a CCD detector), under excitation wavelength of 532 nm and the intensity of ca. 10 mW. The acquisition time was set at 30 s. Precise determination of oxide layers' hardness, Young's modulus, elastic and plastic energy was realized with nanoindentation mechanical tests (NANOTEST VENTAGE MICRO MATERIALS Ltd.). Bioactivity response of the titanium substrates was evaluated by 14 days Kokubo test using *c-SBF2* solution. It was found that the hybrid oxidation method (FB+PVD) leads to formation of tight, homogeneous thin TiO_2 layer, which highly improves the bioactivity of titanium surface in the aspect of biomedical applications.

3. Results and Discussion

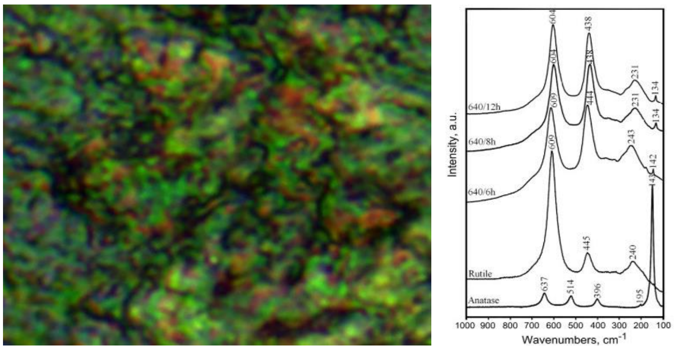
Titanium oxidation realized by two-stage hybrid process (FB+PVD) allowed to produce strength substrates with rutile and anatase TiO_2 thin layer at the top surface. First stage oxidation process conducted in fluidized bed (FB), allowed to obtain $Ti_\alpha(O)$ diffusion layer with thickness of 11 μm and ca. 2 μm nano-porous TiO_2 oxide layer. Saturation of titanium with oxygen atoms leads to strengthening of substrate matrix and improves its hardness. Furthermore, fine grain diffusion zone under a nano-porous oxide layer aims to reduce the stress gradient between matrix and TiO_2 layer. Second stage oxidation process was PVD magnetron sputtering, which result in a deposition of a thin TiO_2 oxide layer with thickness of ca. 0.8 – 1 μm. The plasma interaction with the FB substrate involves continuous bombardment of nano-porous TiO_2 and enhances local heat transfer to control chemical reactions (physisorption) when forming thin TiO_2 PVD layers. Hybrid oxidation also produced stable and fine FB TiO_2 / PVD TiO_2 interface with thickness of ca. 600 – 620 nm (Figure 1.)



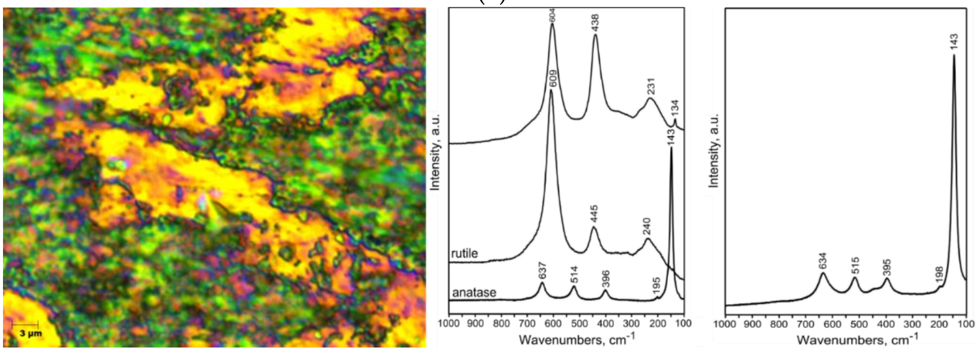
(c)

Figure 1. SEM / STEM images of titanium substrate microstructure and interface after hybrid oxidation (**a**) FB 640 °C / 8 h, (**b**) FB + PVD magnetron sputtering (**c**) FB TiO_2 / PVD TiO_2 interface

At the interface zone there are visible areas of nano-pores size which are free gaps for further anchoring of the TiO_2 layers deposited by PVD method. The next step of the research was substrates surface morphology and phase analysis conducted by Confocal Laser Scaning Microscopy and Raman spectroscopy (Figure 2).



(**a**)



(**b**)

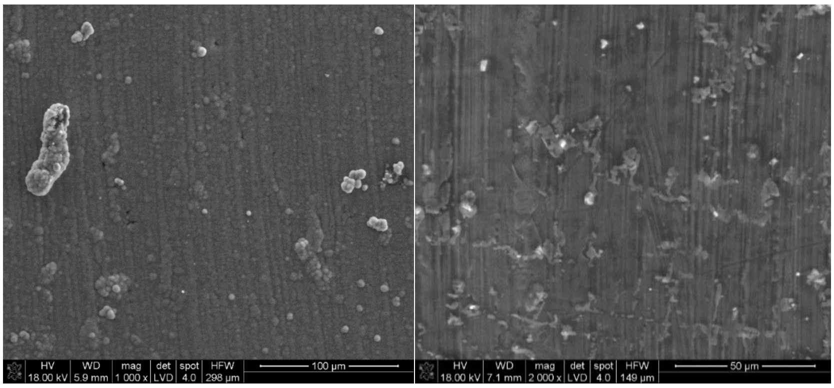
Figure 2. Confocal Laser Scanning Microscopy image and Raman spectra of titanium surface after hybrid oxidation, (**a**) FB 640 °C / 8 h, (**b**) FB + PVD magnetron sputtering.

Raman spectra obtained for titanium after FB oxidation showed the presence of the strongest peaks coming from the rutile. Hardly noticeable bands located at wave numbers of 143-146 cm^{-1} were obtained for anatase phase. However, hybrid oxidation FB+PVD showed the presence of TiO_2 rutile (wavenumbers: 604 cm^{-1}, 438 cm^{-1} and 231 cm^{-1}) and anatase visible band in the range of wavenumbers 143 cm^{-1}, 395 and 515 cm^{-1}. In addition, it was also observed that the bands are shifted towards lower wavenumbers, suggesting the occurrence of compressive stresses in the TiO_2 thin layer. The rutile phase of TiO_2 layers plays an important role in inducing the apatite deposition as a result of the crystal lattice matching between rutile and apatite. In fact there are some literature data which shows biomedical properties of anatase, including also author's previous works [25,26]. Author tries to define and precisely indicate the favorable phase share of the rutile and anatase titanium oxides mixture at the surface, which is promising to has a great influence on bioactive behavior of the substrates. Such phase gradient (between rutile and anatase) has a great influence on osteogenesis and bioactivity of titanium substrates. The next step of the research was nanomechanical investigation of the PVD thin TiO_2 oxide layer. The results showed a favorable strength properties of the layers. Series of indentations (in nano and micro scale) was performed on pure titanium (raw substrates) and the specimens after hybrid oxidation. Results of nanoindentation tests are shown in Table 2.

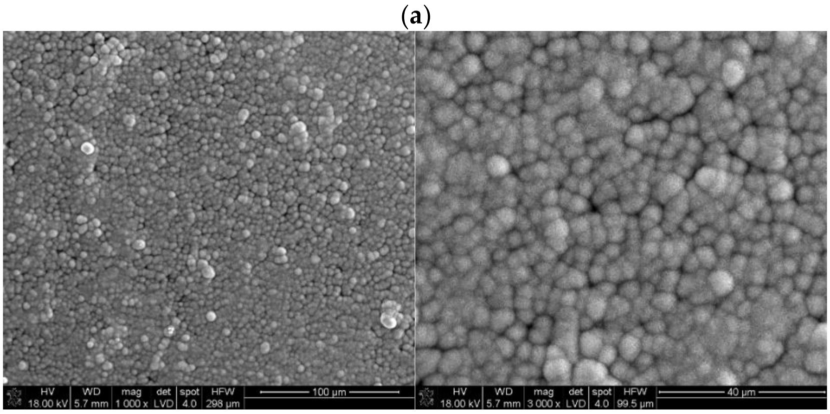
Table 2. Nanoindentation test results of titanium substrates before and after hybrid oxidation (FB + PVD).

Substrate Type	Hardness, H [GPa]		Reduced Young's Modulus, E_R [GPa]		Calculated Young's Modulus, E [GPa]		Maximum Depth [nm]		Plastic Depth [nm]	
	Value	SD	Value	SD	Value	SD	Value	SD	Value	SD
Titanium Grade 2 (ASTM 8348)	9.33	4.14	160.00	60.30	148.34	55.91	204.08	57.41	167.17	54.36
	Value	SD	Value	SD	Value	SD	Value	SD	Value	SD
Titanium after hybrid oxidation FB+PVD	15.21	6.04	281.83	87.79	261.28	81.39	144.90	28.87	119.20	27.37

Results allowed finding a correlation between mechanical parameters measured in nano and micro-scale for the substrates. Special attention was devoted to the mechanical properties of the FB+PVD interface which plays a crucial role in the integrity of the whole hybrid system. Nanoindentation hardness and Young's modulus measured for the FB+PVD TiO_2 were H= 15.21 GPa and E = 261 GPa, which are slightly higher values than the results of sputtered TiO_2 layers reported in the literature [27]. Nanoindentation results confirmed that hybrid oxidation affects the improvement of titanium surface hardness and strength. From the application as biomaterials point of view of obtained substrates it is necessary to determine their bioactivity. Such important results were obtained after the 14 days Kokubo test in SBF [28,29] (Figure 3).



(**a**)



(**b**)

Figure 3. SEM image of hydroxyapatite growth effect on titanium substrates after hybrid oxidation – 14 days SBF Kokubo test, (**a**) FB 640 °C / 8 h, (**b**) FB + PVD rutile + anatase phase.

Intensive growth of globular hydroxyapatite compounds was visible at the surface of FB+PVD TiO_2 thin rutile / anatase layers. Such improvement in biochemical activity was reached both through stabilization and reducing of stresses at FB TiO_2 / PVD TiO_2 interface, and tailoring of the TiO_2 phase composition at the surface. Kokubo test results has confirmed that the hybrid oxidation significantly enhances the bioactivity and allows for biofunctional modification of titanium substrates.

4. Conclusions

A. Diffusion oxidation in a fluidized bed FB leads to formation of a highly defected Tiα(O) diffusion zone with good strength properties and the nano-porous TiO_2. Such system plays role as a foundation for subsequent deposition of thin TiO_2 layer by PVD magnetron sputtering.

B. The hybrid oxidation treatment applies two types of the surface activation, I: mechanical as an impact of an aeromechanical factor in FB; II: sputtering with simultaneous oxidation by PVD. Activation increases the number of active centers, and enhances oxygen mass transport finally to form a homogenous thin TiO_2 layers. The layers are characterized by high level of homogeneity and resistant to cracking and delayering.

C. In hybrid oxidation, the interface between nano-porous FB TiO_2 and PVD TiO_2 has a favorable state of stress and influences in further formation of a bioactive rutile and anatase mixture which improves the rate of osseointegration.

D. The presented hybrid oxidation is a promising surface treatment for biomedical applications, indicating the directions of forming bioactive layers on titanium substrates. The solution corresponds with the new trends in biomaterials and surface engineering to combine different processing techniques in order to improve the implants and medical devices.

5. Patents

Patent no PL 221053 Method for modifying the surface layer of titanium alloy implants P. Podsiad, J.J. Jasinski, J. Jasinski, R. Czyz.

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Conflicts of Interest: The author declares no conflict of interest.

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