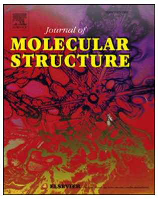
Journal of Molecular Structure xxx (2016) 1–7

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc



Effect of hybrid oxidation on the titanium oxide layer's properties investigated by spectroscopic methods

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ARTICLE INFO

Article history:
Received 30 December 2015
Received in revised form
18 February 2016
Accepted 22 February 2016
Available online xxx

Keywords:
Titanium Grade 2
Hybrid oxidation
Bioactivity
Oxide coating
Hydroxyapatite

ABSTRACT

In this work the study of hybrid Ti Grade 2 during oxidation using FADT – fluidized bed atmospheric diffusive treatment and PVD – magnetron sputtering have been investigated. Additionally, the influence of the oxidation method on the change in the mechanism of oxygen transport to the substrate have been discussed (phenomenon responsible for the improvement of bioactivity). Presented method consists in forming the titanium surface layer saturated with oxygen due to the diffusion and deposition of a thin homogeneous oxide coating on the Ti surface. Discussed processes diminish the surface roughness and increase bio-compatibility of the surface, which results in easier hydroxyapatite cluster deposition. The diffusion process was conducted on Al_2O_3 fluidized bed, with air as the fluidizing factor at 913 K for 8 h. The deposition of the oxide coatings were carried out with magnetron sputtering, with the use of a TiO_2 target at a pressure of 3×10^{-2} mbars and power of 350 W. To evaluate the effects of hybrid oxidation and to determine the mechanism of oxygen transport, the following research methods have been applied: spectroscopy (GDOS, SIMS, RS), microscopic methods (SEM-EDS, SEM-EBSD, TEM-EFTEM), X-ray tests (μ-XRD, GID). Obtained test results were used to identify the type of oxide coatings, to assess the thickness of the layers and to study the influence of crystallographic orientation on oxygen transport and concentration in the surface layer and in the oxide coating. It has been found that the formation of oxide coatings created by using the hybrid method (FADT + PVD leads to a change in oxygen concentration in the substrate due to introduced defects. This phenomenon is in opposition to the conventional methods such as: electrochemical or laser oxidation. In contrast, forming a tight homogeneous oxide coating on Ti surface improves the biocompatibility, which is particularly important in the context of biomedical applications.

1. Introduction

Increasing materials' biocompatibility has always constituted a challenge for biomedical engineering. In order to improve titanium properties for biomedical applications many methods of forming oxide coatings are used, including, inter alia, electrochemical methods (anodizing), physical vapour deposition (PVD) and laser methods (laser ablation). Oxide coatings obtained with the use of the methods mentioned, however, have small thickness, and in the case of coatings formed by the electrochemical method, they do not always have good adhesion, which depends on many factors, including titanium surface preparation for the processes [1–3]. These methods, due to the conditions of physical and chemical interaction between the atmosphere and the surface, heat transport, and surface defects, have very limited influence on oxygen diffusion processes towards the surface layer. Thus, it is difficult to obtain the following arrangement: TiO_2 oxide coating/solid solution of oxygen in $Ti_\alpha(O)$ titanium/Ti_αsubstrate. The analysis of titanium use in biomedicine shows that favourable properties are typical of substrates obtained by diffusion methods, including oxidizing in a fluidized bed [4,5]. This method of titanium oxidation is used as one of the ways of surface protection and improves

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http://dx.doi.org/10.1016/j.molstruc.2016.02.080

Please cite this article in press as: J.J. Jasinski, et al., Effect of hybrid oxidation on the titanium oxide layer's properties investigated by spectroscopic methods, Journal of Molecular Structure (2016), http://dx.doi.org/10.1016/j.molstruc.2016.02.080

Table 1
The chemical composition of Titanium Grade 2, % mass.

Material	Chemical composition, % mas.					
Ti Grade 2	O	N	C	H	Fe	Ti
	0.20	0.03	0.10	0.015	0.30	Balance

titanium corrosion properties, however, methods to improve the substrate's biocompatibility are still being sought, in order to increase the activity of compounds having properties that enhance tissue regeneration, for example hydroxyapatite [6–8]. The phenomenon of oxygen diffusion to the titanium substrate occurs by means of an interstitial mechanism with diffusion pathways resulting from the fluidized bed grain material continuously causing surface defects. Consequently, this enhances the change in the oxygen concentration profile, with the formation of the diffusion zone of oxygen solid solution in $Ti_{\alpha}(O)$ and a porous TiO_2 oxide coating (rutile) of a favourable substrate – coating stress state [9]. Such titanium substrate obtained after FADT (fluid atmosphere diffusive treatment), with porous areas, has limited use in terms of improving the biocompatibility due to the insufficient adhesion of hydroxyapatite compounds. Therefore, there is a need to carry out a research aimed at forming a homogeneous, non – porous oxide coating, ensuring the adhesion of biologically compatible compounds. Therefore, the research carried out aims to develop such a novel Ti Grade 2 surface layer, whose surface zone is a solid solution of oxygen in $Ti_{\alpha}(O)$ saturated by means of diffusion, and the outer TiO_2 oxide coating is produced by magnetron sputtering (PVD). Such an innovative solution is a hybrid combination of coatings which ensures a synergistic increase in essential material properties, crucial from the point of view of the biocompatibility of the implant – tissue system. The scope is mainly to investigate the interface between $Ti_{\alpha}(O)$ and PVD TiO_2 formed oxide and formation mechanism of TiO_2 anatase phase that significantly enhance biocompatibility of the substrate. Mentioned multi-combination of these techniques might is a new approach in surface engineering for surface properties improvement of titanium elements and is highly desirable in the aspect of biomedical applications. The properties mentioned are mainly: the reduction in the stress gradient between the diffusive zone and the tight and homogeneous PVD coating, with a simultaneous morphology improvement. Combining the methods in the hybrid system suggested allows a synergistic improvement in the surface effects affecting the intensity of the subsequent deposition of hydroxyapatite compounds. The selection of methods (FADT + PVD) in a hybrid system makes it possible to use the advantages of spontaneous mechanical surface activation, as a result of the impact of an aeromechanical factor in the fluidized bed, which occurs due to the recurrent defecting of the substrate surface with simultaneous oxidation. This, in turn, together with an increase in the number of active centres, determines the subsequent oxygen mass transport to form a TiO_2 oxide coating. However, using the PVD method – magnetron sputtering, ensures obtaining the oxide coating morphology favourable to the nucleation of biocompatible compounds (HAp).

2. Material and methods

For oxidation processes, titanium GRADE 2 was used in the form of cylindrical samples of 10-mm-length, cut out from a Ø = 20 mm rod. The chemical composition of the material is presented in Table 1.

The titanium used in the oxidation tests had a Ti_{α} single – phase structure with bands after plastic treatment. The surface of the samples before oxidation was mechanically activated in the process of sanding (a mixture of $Al_2O_3 + ZrO_2 + Ti$). Diffusive oxidation (FADT) of the titanium substrate was carried out in a fluidized bed reactor with Al_2O_3 as grain material at 913 K for 8 h. The fluidizing factor was air, in which oxygen was also a carrier of diffusion atoms. After oxidation in a fluidized bed, oxidation processes were conducted with the use of magnetron sputtering (PVD), using a TiO_2 target at a pressure of 3×10^{-2} mbar, in Ar atmosphere. To assess the mechanism and intensity of oxygen transport to the titanium Grade 2 surface layer, the following tests were carried out: the Ti layer oxygen concentration change by means of glow discharge optical spectroscopy (GDOS) and secondary ion mass spectroscopy (SIMS), microscopic structural studies and maps of oxygen concentration in Ti Grade 2 (SEM-EDS, SEM-EBSD, TEM-EFTEM), a study of TiO_2 phases with the use of x-ray (μ-XRD) and Raman Spectroscopy (RS). The test

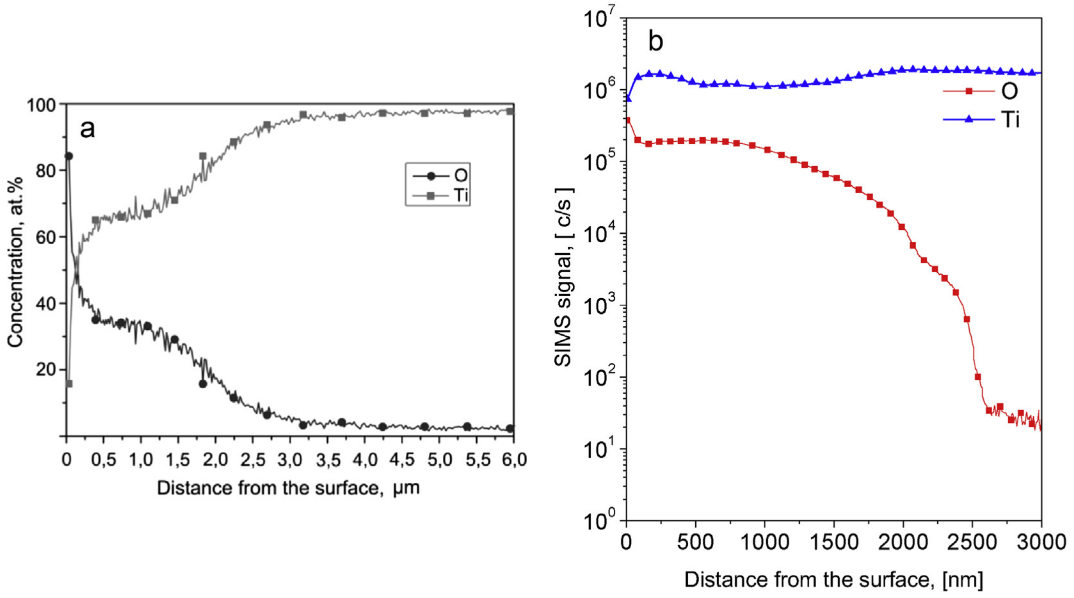

Fig. 1. Oxygen concentration distribution a) oxidation in a fluidized bed (FADT) 913 K (GDOS), 8 h b) hybrid oxidation FADT + PVD (SIMS).

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