PROCEEDINGS

PROCEEDINGS
of the 2nd International Conference on
Advanced Production and Processing
May, 2023.

Title:
Proceedings of the 2nd International Conference on Advanced Production and Processing publishes abstracts from the following fields: Innovative Food Science and Bioprocesses, Nutraceuticals and Pharmaceuticals, Sustainable Development, Chemical and Environmental Engineering, Materials Design and Applications.

Publisher:
University of Novi Sad, Faculty of Technology Novi Sad,
Bulevar cara Lazara 1, 21000 Novi Sad, Serbia

For publisher:
prof. Biljana Pajin, PhD, Dean

Editor-in-Chief:
Prof. Zita Šereš, PhD

Design and Printing Layout:
Saša Vulić

CIP - Каталогизација у публикацији
Библиотеке Матице српске, Нови Сад

658.5(082)

INTERNATIONAL Conference on Advanced Production and Processing (2 ; 2023 ; Novi Sad)
Proceedings of the 2nd International Conference on Advanced Production and Processing ICAPP 2022, Novi Sad [Elektronski izvor] / [editor-in-chief Zita Šereš]. - Novi Sad : Faculty of Technology, 2023

Način pristupa (URL): https://www.tf.uns.ac.rs/download/icapp-2022/icapp-proceedings.pdf. - Opis zasnovan na stanju na dan 1.6.2023. - Nasl. s naslovnog ekrana. - Bibliografija uz svaki rad.

ISBN 978-86-6253-167-4

а) Технологија -- Производња -- Зборници

COBISS.SR-ID 117323785

Materials Design and Applications

The surface characterization of the anodized ultrafine-grained Ti-13Nb-13Zr alloy

Dragana R. Barjaktarević*[1]*, Marko P. Rakin*[1]*, Bojan I. Međo*[1]*, Zoran M. Radosavljević*[2]*,
***Veljko R. Đokić*[3]**

[1] *University of Belgrade, Faculty of Technology and Metallurgy, Karnegijeva 4, 11120 Belgrade, Serbia, dbarjaktarevic@tmf.bg.ac.rs, bmedjo@tmf.bg.ac.rs, marko@tmf.bg.ac.rs*

[2]*Lola Institute, Kneza Višeslava 70a, 11030 Belgrade, Serbia, z.radosavljevic@mont-r.rs*

[3]*Innovation Centre of the Faculty of Technology and Metallurgy, Karnegijeva 4, 11120 Belgrade, Serbia, vdjokic@tmf.bg.ac.rs*

Abstract

Titanium alloys are metal materials widely used in medicine owing to their suitable characteristics such as low density, good corrosion resistance and biocompatibillity. High biocompatibility of the titanium alloy results from the creation of a spontaneous oxide layer with good adhesion and homogeneous morphology. In order to improve characteristics of the metallic materials for application in medicine, electrochemical methods that enable surface nanostructured modification are extensively used, and one of these methods is electrochemical anodization which makes it possible to obtain a nanostructured oxide layer composed of nanotubes on the surface of the metal material. The tested material was ultrafine-grained Ti-13Nb-13Zr (UFG TNZ) alloy obtained by the severe plastic deformation (SPD) processing using the high pressure torsion (HPT) process. Nanostructured oxide layer on the titanium alloy was formed by electrochemical anodization during the time period from 30 to 120 minutes. Characterization of the surface morphology obtained during different times of electrochemical anodization was done using scanning electron microscopy (SEM), while the topography and surface roughness of the titanium alloy before and after electrochemical anodization was determined using atomic force microscopy (AFM). Scratch test was used to determine the cross profile of the surface topography. Electrochemical anodization led to the formation of a nanostructured oxide layer on the surface of the titanium alloy. The obtained results indicated strong influence of the electrochemical anodization time on the oxide layer morphology - with its increase the diameter of the nanotubes increases too, while the wall thickness of nanotubes decreases. Also, electrochemical anodization led to an increase in the surface roughness.

Keywords: Titanium alloy for biomedical application, High pressure torsion process, Electrochemical anodization, Surface morphology, Surface roughness

1. Introduction

The main goal of developing materials for use in medicine is to achieve the desired material properties, primarily mechanical and physical, for which thermomechanical processing procedures and the addition of alloying elements are used. Contemporary research in the field of metallic biomaterials is focused on the possibility of converting conventional macroparticle biomaterials into submicron and nanoparticle biomaterials while achieving adequate mechanical, physical, biological and corrosion properties. Numerous researches are focused on the process of forming ultrafine-grained and nanocrystalline structures (grain size less than 100 nm), because it has been shown that such structures are characterized by higher tensile strength, better biocompatibility and corrosion stability, as well as better wear resistance [1,2]. Severe plastic deformation (SPD) uses different methods for refining material structure by reducing the grain size and for conversion of a coarse-grained structure into an ultrafine-grained structure or a nanostructure [3-5]. Several different SPD procedures are available, but one of the most effective one is the high-pressure torsion (HPT) processing, that enables small grains and high strength to be obtained, as it is shown in [6]. HPT apparatus consists of two anvils, Fig 1. A thin disc is pressed between two anvils, under high pressure, and the rotation of the one of the anvils causes large shear deformations of the material.

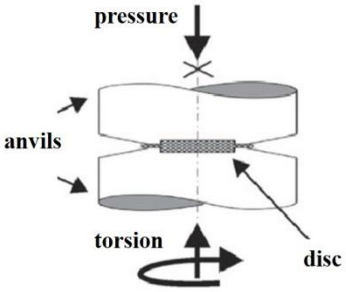


Figure 1. HPT apparatus [7]

The behavior of biomaterials in the human body depends on its biocompatibility and surface properties. For this reason, biomaterials often require surface modification in order to optimize the properties of the implants and increase their bioactivity when connecting with the natural surrounding tissue. There are various procedures that can be used to modify the surface of metal biomaterials (including bringing the material to an ultrafine-grained structure) and which lead to an improvement in their properties compared to conventionally made implants. The primary need for surface nanostructural modifications in titanium-based materials, apart from better and faster connection with bone tissue, is also due to the improvement of the degree of osseointegration, biocompatibility, as well as resistance to corrosion and wear. Chemical methods for surface modification of materials are used in order to improve biocompatibility, corrosion resistance, wear resistance and contamination removal [8]. Some of the most commonly used chemical methods are chemical treatments, electrochemical treatments, i.e. electrochemical anodization (anodic oxidation), sol-gel process and chemical vapor deposition [9-11]. In this work, electrochemical anodization was used to modify the surface of the titanium alloy. The basic characteristics of the modified surface of the titanium alloy obtained by electrochemical anodization are shown in table 1. As a result of electrochemical anodization, a nanostructured oxide layer composed of nanotubes is obtained. The morphology and structure of the obtained nanostructured oxide layer depends on the characteristics of the substrate, the composition of the electrolyte and the parameters of the electrochemical anodization procedure [12,13].

Table 1. Main characteristics of the modified surface of the titanium alloy obtained by electrochemical anodization

Electrochemical andization (Anodic oxidation)	Formation of a nanostructured oxide layer composed of TiO_2-based nanotubes with a thickness of 10 nm to 40 µm	Formation of a specific topography of the surface, improvement of corrosion resistance, biocompatibility, bioactivity, reduction of the value of the surface modulus

The most significant advantage of the electrochemical anodization procedure is the creation of a homogeneous nanotubular oxide layer. The shape of the nanotubular oxide layer (diameter, length, and thickness of the nanotubes) can be controlled using electrochemical anodization parameters [14-16]. TiO_2 nanotubes of different diameters (from 15 nm to 300 nm) and different lengths can be formed during the process of electrochemical anodization of titanium or titanium alloys.

It has been shown that the nanostructured surface of titanium alloy can be formed by applying electrochemical anodization, but the question remains open as to the morphology of ultrafine-grained titanium alloys obtained by high pressure torsion (HPT) process.

2. Materials and methods

The tested material was ultrafine-grained Ti-13Nb-13Zr (UFG TNZ) alloy obtained by the SPD processing using the HPT process. The HPT process was done by rotating one of the anvils with speed of 0.2 rpm at a pressure of 4.1 GPa. Nanostructured oxide layer on the UFG TNZ alloy was formed by electrochemical anodization during 60 and 90 minutes. Electrochemical anodization was performed using a system of two electrodes: platinum and a sample of the UFG TNZ alloy as working electrode. It was conducted at a voltage of 25V, while 1M H_3PO_4 + 0.5 wt. % NaF was chosen as the electrolyte. The PEQLAB EV 231 device was used to supply power during the electrochemical anodization process.

The scanning electron microscopy (SEM) was used to characterize the nanostructured oxide layer morphology. The TESCAN MIRA3 XMU microscope at a voltage of 20 keV was used for SEM analysis. The topography and surface roughness of the titanium alloy before and after electrochemical anodization was determined by atomic force microscopy (AFM) with NanoScope 3D (Veeco, USA) microscope operated in tapping mode in ambient conditions.

The scratch test was performed on nanoindenter G200, Agilent Technologies, using as an indenter Berkovich-type diamond tip. Scratch length was 500 μm and applying an increasing load up to 40 mN, Fig. 2. In this study, scratch test was used to determine the cross profile of the surface topography.

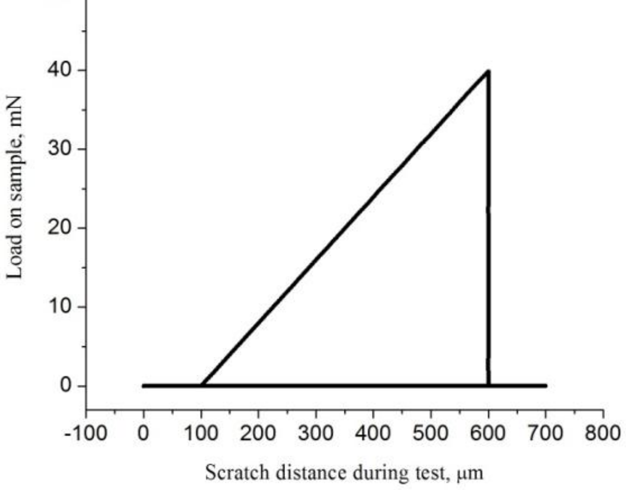


Figure 2. Applied load during scratch test

3. Results and Discussion

Fig. 3. presents morphology of the surface of the UFGG TNZ alloy after electrochemical anodization for 60 and 90 minutes. After 60 minutes of electrochemical anodization, a nanoporous oxide film was formed on the surface of the UFG TNZ alloy, Fig 3 (a). The nanotubular oxide layer was formed after a procedure lasting 90 minutes, Fig 3 (b). During the shorter process of electrochemical anodization, nanotubes were formed and connected to each other, while during the longer process, nanotubes were formed and separated from each other due to dissolution.

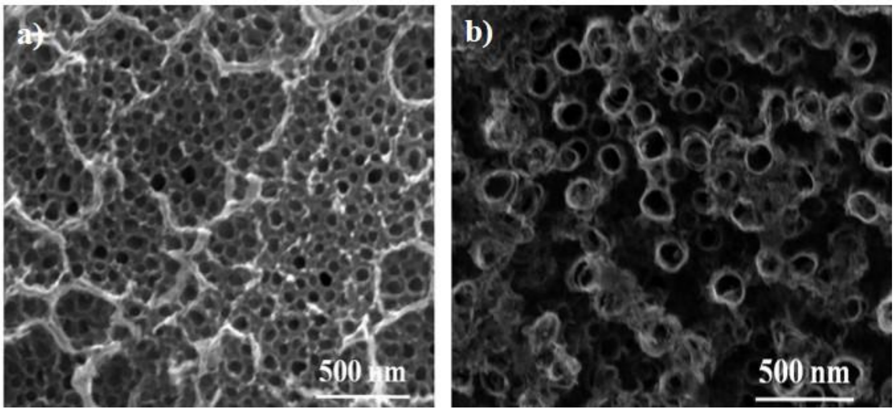


Figure 3. Morphology of the surface of the UFG TNZ alloy after electrochemical anodization for (a) 60 and (b) 90 minutes

The mean value of the nanotube diameter (obtained after 30 measurements) after 60 minutes of electrochemical anodization was 56.22 nm, while after 90 minutes of electrochemical anodization it increased to 90.17 nm. On the other hand, the mean value of the nanotube wall thickness (obtained after 30 measurements) decreased from 22.20 nm to 19.54 nm with increasing anodization time. The existence of the influence of the anodizing time on the dimensions of the nanotubes has been shown, so that with increasing time, the diameter increases too while the thickness of the nanotubes decreases. Also, increasing anodizing time led to the formation of the more homogeneous oxide layer on the surface, Fig 3 (b).

As we presented in our previous paper [17] the SEM side-view image of the oxide layer created on the UFG TNZ during 60 minutes showed that nanotubes were parallel on the surface with an average thickness of 1.63 nm, while it was theoretically known that increasing the anodizing time leads to an increase in the length of the nanotubes [18]. Further, HPT process, as the method for obtaining ultrafine-grained microstructure, leads to the formation of smooth walls.

AFM was used to characterize the surface topography of the UFG TNZ alloy before and after electrochemical anodization, and results of the analysis are presented in Fig 4.

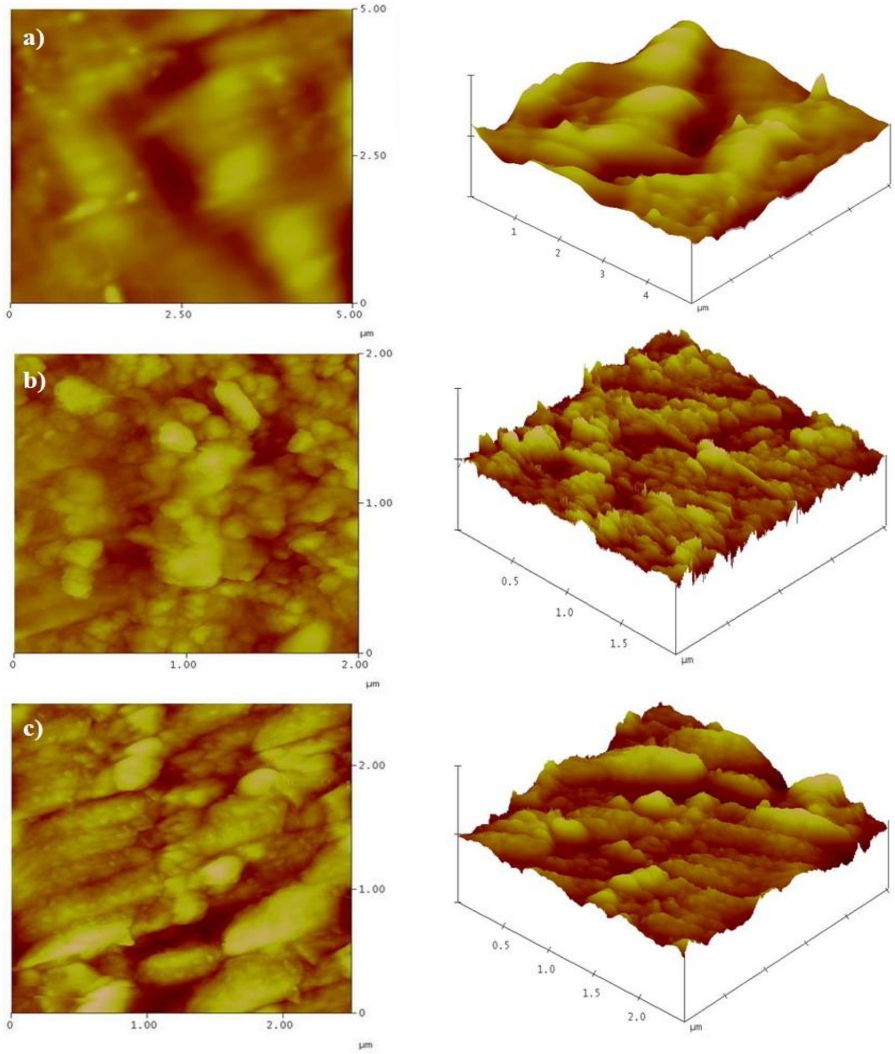


Figure 4. 2D and 3D AFM images of the UFG TNZ alloy (a) before anodization (5x5x0.1) and after anodization for (b) 60 (2.5x2.5x0.4) and (c) 90 (2.5x2.5x0.4) minutes

Table 2. presents values of the surface roughness (RMS-root mean square average of height deviations (expressed in nm)) of the UFG TNZ alloy before and after electrochemical anodization for 60 and 90 minutes.

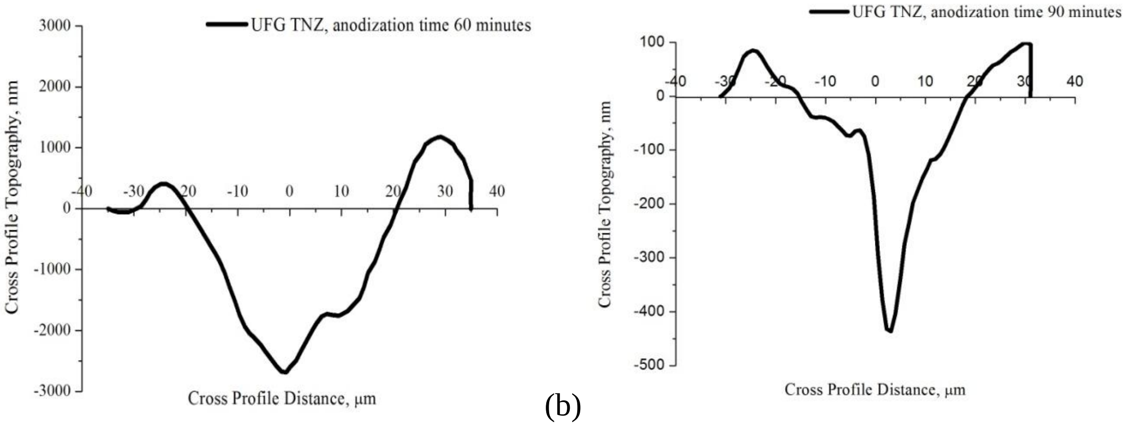
The obtained results showed that the process of electrochemical anodization resulted in the creation of a rough topography of the surface of the UFG TNZ alloy. The UFG TNZ alloy anodized for 60 and 90 minutes is characterized by a typical rough surface topography compared to the base alloy surface which has a wavy topography, Fig 4.

The anodized ultrafine grained alloy has an order of magnitude higher roughness value in comparison to the alloy before anodization, Table 2. The results show that increasing the time of electrochemical anodization also increases the roughness of the alloy as a result of increasing the size and number of pores [19].

Table 2. Surface roughness values before and after electrochemical anodization

Materials	Anodizing time, min	RMS, nm
UFG TNZ	/	3.61
	60	33.39
	90	34.15

Fig. 5. presents the cross profile of the surface topography of UFG TNZ alloy after electrochemical anodization for 60 and 90 minutes obtained after scratch test. The surface roughness of UFG TNZ after electrochemical anodization for 90 minutes is higher than for 60 minutes, as shown in Fig. 5, and the texture parameter is 61 μm in diameter for alloy after anodization for 90 minutes and 52.9 μm for alloy after anodization for 60 minutes.



(a) (b)

Figure 5. The cross profile of the surface topography of UFG TNZ alloy after electrochemical anodization for (a) 60 and (b) 90 minutes, obtained after scratch test

4. Conclusion

It can be concluded that electrochemical anodization is a suitable method for the formation of nanostructured surface on the titanium alloy. The roughness of the nanostructured surface is greater compared to the bare surface of UFG TNZ alloy. It indicates that the UFG TNZ alloy with nanostructured surface would be more suitable for medical application, because of better contact of the modified surface with surrounding tissue and their adhesion. Also, it can be said that the anodizing time of 90 minutes is more suitable for using compared to 60 minutes, because this anodizing time leads to the formation of a homogeneous nanotubular oxide layer with larger roughness.

Increasing of anodizing time leads to the increase of the surface roughness and therefore to the increase of cell adhesion in the human body. In our previous paper [17] we showed that increasing anodizing time led to the improvement of corrosion resistance in the artificial saliva, simulating the oral environment. From everything analyzed so far, we concluded that the deterioration of the surface properties occurred during the formation of a nanostructured oxide layer at a shorter anodizing time. The previous paper also analyzed morphology of the nanostructured oxide layer and dimension of the nanotubes obtained for the anodizing time of 120 minutes, but the surface characterization after this anodizing parameter will be considered in the future.

Acknowledgements

This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Contracts No. 451-03-68/2022-14/200135). The authors gratefully acknowledge Dr. Sanja Stevanović from the Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Serbia, for performing the AFM measurements and Dr Anton Hohenwarter from the Erich Schmid Institute of Material Science, Leoben, Austria, for the preparation of the UFG TNZ alloy.

References

1. Y. Estrin, A. Vinogradov, Extreme grain refinement by severe plastic deformation: A wealth of challenging science, Acta Mater, 61(2013) 780-786.

2. I. Dimić, I. Cvijović-Alagić, B. Volker, A. Hohenwarter, R. Pippan, Đ. Veljović, M. Rakin, B. Bugarski, Microstructure and metallic ion release of pure titanium and Ti-13Nb-13Zr alloy processed by high pressure torsion, Mater Des, 5 (2016) 340-347.
3. I. Turkyilmaz, Implant Dentistry - A Rapidly Evolving Practice, In Tech (2011) 57-82.
4. H. Yilmazer, M. Niinomi, M. Nakai, K. Cho, J. Hieda, Y. Todaka, T. Miyazaki, Mechanical properties of a medical β-type titanium alloy with specific microstructural evolution through high-pressure torsion, Mater Sci Eng C, 33 (2013) 2499-2507.
5. J. Wongsa-Ngam, M. Kawasaki, T. Langdon, A comparison of microstructures and mechanical properties in a Cu–Zr alloy processed using different SPD technique, J Mater Sci, 48 (2013) 4653-4660.
6. G. Crawford, N. Chawla, K. Da, S. Bose, A. Bandyopadhya, Microstructure and deformation behavior of biocompatible TiO_2 nanotubes on titanium substrate, Acta Biomater, 3 (2007) 359-367.
7. A. Hohenwarter, R. Pippan, Fracture and fracture toughness of nanopolycrystalline metals produced by severe plastic deformation, Philo Trans A, Published by Royal Society, 2014.
8. M. Kulkarni, A. Mazare, P. Schmuki, A. Iglič, Biomaterial surface modification of titanium and titanium alloys for medical applications, Nanomedicine, Publisher: One Central Press, 2014.
9. T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino, K. Niihara, Formation of titanium oxide nanotube, Lang, 14 (1998) 3160-3163.
10. C. Tsai, N. Nian, H. Teng, Mesoporous nanotube aggregates obtained from hydrothermally treating TiO_2 with NaOH, Appl Surf Sci, 253(2006) 1898-1902.
11. D. Barjaktarević, I. Cvijović-Alagić, I. Dimić, V. Đokić, M. Rakin, Anodization of Ti-based materials for biomedical applications: A review, Metall Mater Eng, 22 (2016) 129-143.
12. M. Hu, P. Lai, M. Bhuiyan, C. Tsouris, B. Gu, M. Paranthaman, J. Gabitto, L. Harrison, Synthesis and characterization of anodized titanium-oxide nanotube arrays, J Mater Sci, 44 (2009) 2820-2827.
13. H. Park, H. Kim, W. Choi, Characterizations of highly ordered TiO_2 nanotube arrays Obtained by anodic oxidation, Trans Electro Electron Mater, 11 (2010) 112-115.

14. K. Kim, N. Ramaswamy, Electrochemical surface modification of titanium in dentistry, Dent Mater J, 28 (2009) 20-36.
15. J. Hernández-López, A. Conde, J. Damborenea, M. Arenas, Electrochemical response of TiO_2 anodic layers fabricated on Ti-6Al-4V alloy with nanoporous, dual and nanotubular morphology, Corr Sci, 112 (2016) 194-203.
16. A. Tan, B. Pingguan-Murphy, R. Ahmad, S. Akbar, Review of titanium nanotubes: Fabrication and cellular response, Ceramics Inter, 38 (2012) 4421-4435.
17. D. Barjaktarevića, V. Djokića, J. Bajata, I. Dimića, I. Cvijović-Alagićb, M. Rakina, The influence of the surface nanostructured modification on the corrosion, resistance of the ultrafine-grained Ti–13Nb–13Zr alloy in artificial saliva, Theor and Appl Fract Mech 103 (2019) 102307.
18. A. Ghicov, H. Tsuchiya, J. Macak, P. Schmuki, Titanium oxide nanotubes prepared in phosphate electrolytes, Electrochem Commun, 7 (2005) 505-509.
19. M. Manjaiah, R. Laubscher, Effect of anodizing on surface integrity of grade 4 titanium for biomedical applications, Surf Coat Technol, 310 (2017) 263-272.