G. GAŁUSZKA, M. MADEJ, D. OZIMINA, J. KASIŃSKA, R. GAŁUSZKA

ISSN 0543-5846
METABK 56(1-2) 191-194 (2017)
UDC – UDK 669.295:615.47:620.17:620.18=111

THE CHARACTERISATION OF PURE TITANIUM FOR BIOMEDICAL APPLICATIONS

Received – Prispjelo: 2016-04-10
Accepted – Prihvaćeno: 2016-08-12
Preliminary Note – Prethodno priopćenje

The paper presents results of research on the use of pure titanium medical implants, dental and orthopedics - as pins hip replacements. The properties of metal biomaterials, including their hardness, determine the usefulness of the material and are one of the criteria for its use. They depend on their chemical composition and structure. Studies included the observation of the microstructure and mechanical properties of pure titanium. The observations surface were carried out using a scanning electron microscope SEM. The optical profiler was used to depict the geometric structure of the surface, and to carry out the nanoindentation tests a nano hardness tester was used.

Keywords: pure titanium, biomedical applications, mechanical properties, microstructure, nanoidentation

INTRODUCTION

Implantology is currently one of the fastest growing fields in the area of technical sciences and medicine [1, 2]. Biomaterials used for implants include: hydroxyapatite ceramics, modified carbon materials, composite materials, metals and their alloys (mainly titanium and cobalt). These materials combine permanently with living tissue, or take part in the regeneration [3, 4].

Titanium is common in biomedical applications because of its low density, good mechanical properties, high strength to weight ratio and resistance to corrosion and due to its ability to osseointegration, or a direct structural and functional connection between the living bone and the implant surface [4, 5].

Titanium is used to perform plate osteosynthesis limbs and skull and facial, dental implants, some elements for combinations of contact, implants for cardiac and surgery, otolaryngology and components for reconstruction [2, 6, 7]. During the selection of materials for the manufacture of medical implants in addition to biocompatibility its physico-chemical and mechanical properties are important (Table. 1) [1]. This has importance because of the function functional area where used implants or endoprosthesis. Taking into account the biomechanics - these parts of the body require appropriate parameters (strength, endurance) to fulfill its function [8].

Titanium has a high corrosion resistance, which is related to its high affinity to oxygen and the formation on the metal surface a stable, tightly adherent to the substrate, the passive oxide layer. Titanium has the ability to naturally self-passivate, even in saline [6, 7]. If there is a damage to its surface in direct contact with living tissue (bone or soft) this may then lead to metalosis, inflammatory reactions and, consequently, loosening of the implant.

G. Gałuszka - School of Economics, Law and Medical Sciences in Kielce, Poland
M. Madej, D. Ozimina, J. Kasińska -Kielce University of Technology, Poland
R.Gałuszka, The Jan Kochanowski University in Kielce, Poland

MATERIALS AND METHODS

The samples were prepared in the form of discs with a diameter of 19 mm and a height of 6 mm and a pin diameter of 9 mm and a height of 13 mm titanium grade 4 according to ASTM F67. In order to obtain a small surface it was used roughness of samples in the treatment of abrasive grinding operations, super finishing, lapping and polishing.

The desired surface roughness was obtained by using abrasive processing operations finish grinding and polishing. Polishing grinding wheels were used with a paper weight of 400 to 4 800 in a cooling lubricant emulsion, and then polishing, polishing wheels emulsion diamond of the diamond grains with dimensions of 9 µm to 0,5 µm.

The study was conducted for the samples after grinding and polishing, and $Al2O_3$ samples sandblasted and

Table 1 **The mechanical properties of titanium alloys used for implants [1]**

	Ti	Ti-6Al-4V	Ti-6Al-7Nb	Ti-13Nb-13Zr
Modulus of elasticity E / GPa	105	110 ÷ 114	105	79
Tensile strength R_m / MPa	785	960 ÷ 970	1 024	1 030
Yield strength $R_{p0,2}$ / MPa	692	850 ÷ 900	921	900
Fatigue strength R_z / MPa for 107 series	430	620 ÷ 725	500 ÷ 600	500

chemically etched with 5 % HF + 5 % HNO_3. The observations of surface morphology was performed at the Laboratory of Scanning Electron Microscopy (SEM) and X-ray microanalysis of Kielce University of Technology using a scanning electron microscope JEOL JSM 7100F's with capacity distribution of 1.2 nm. The research included observations of surface topography, and microanalysis points allowed to determine the chemical composition. Geometrical structure of the surface was conducted with the optical test profilometer Talysurf CCI Taylor Hobson Laboratory Measurement of geometrical Kielce University of Technology. It is a non-contact profiler uses a broadband scanning interferometry (coherence correlation interferometry), which allows to obtain high-resolution vertical (Z - axis) 0,1 Å regardless of the magnification.

The measurement results are recorded by a CCD camera with a resolution of 1 024 x 1 024 pixels which causes that a single measurement has more than one million points of measured surface used to generate a 3D image. When measuring 0,33 mm x 0,33 mm area was measured, and the measurement range in the Z axis was 2,2 mm. The device is equipped with an application TalyMap Platinium that allows processing and comprehensive analysis of the data. Complementary information on the topography of test samples have given amplitude parameters: skewness (asymmetry) Sku, and the concentration ratio (kurtosis) Ssk. These parameters are sensitive to the occurrence of local peaks, pits or defects on the surface [9].

Hardness measurements were performed using nanoindentation, consisting of measuring the loading force in a continuous indentation and the recess of the loading and unloading of the test sample [10].

Tests were performed using nanohardness tester of NHT2 Anton Paar. This device is used to designate the micromechanical properties of materials, such as hardness and Young's modulus. After each complete cycle consisting of the loading and unloading of the sample it is plotted a graph load of the indenter as a function of penetration depth displacement - as in Figure 1, where: P - load, h_c - penetration depth, h_f – residual depth, h_c – contact depth, h_{max} – maximal depth, S – contact stiffness.

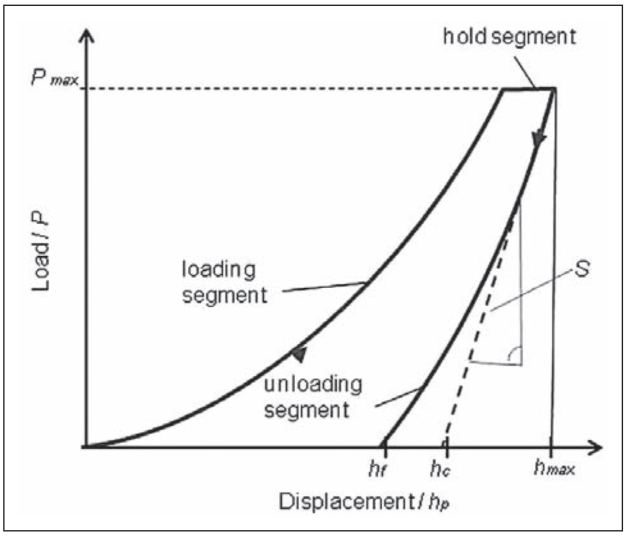


Figure 1 Typical load-penetration depth curve

The analysis of the results was based on the following relationships:

– reduced modulus:

$$\frac{1}{E^*}=\frac{1-\nu^2}{E}-\frac{1-\nu'^2}{E'} \tag{1}$$

Where:

E - modulus of specimen,

E' - modulus of intender

ν - Poisson's ratio.

– stiffness:

$$S=\frac{dP}{dh}=2E^*\frac{\sqrt{A}}{\sqrt{P}} \tag{2}$$

– contact area:

$$A=3\sqrt{3}h_p^2\tan^2 65,3=24,5h_p^2 \tag{3}$$

where: h_p -penetration depth.

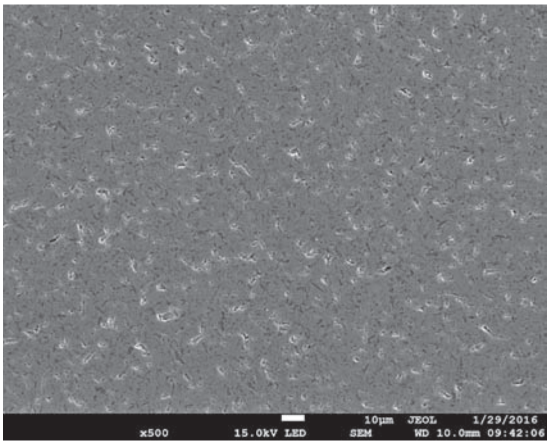
– hardness:

$$H=\frac{P}{24,5h_p^2} \tag{4}$$

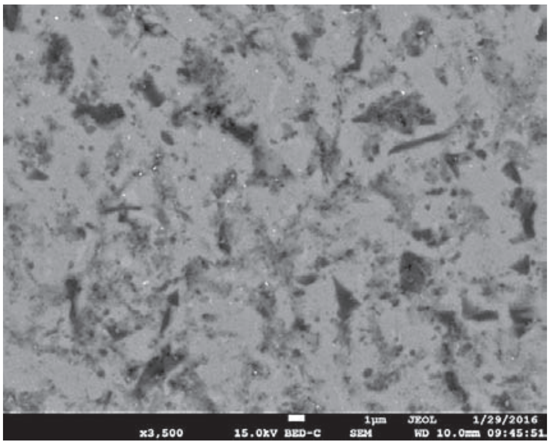
– elastic modulus:

$$E^*=\frac{dP}{dh}\frac{1}{2h_p}\frac{1}{\beta}\sqrt{\frac{\pi}{24,5}} \tag{5}$$

β = 1,034 for Berkovich intender.



a)



b)

Figure 2 SEM: microstructure of polished titanium at magnifications: a) 500 x, b) 3 500 x

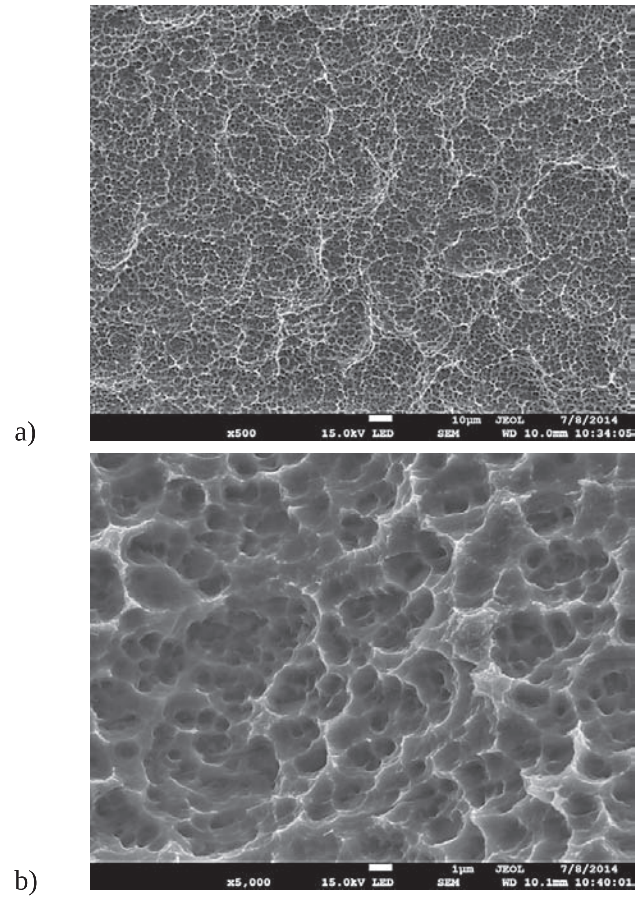


Figure 3 SEM: microstructure of sandblasted and etched titanium at magnifications: a) 500 x, b) 5 000 x

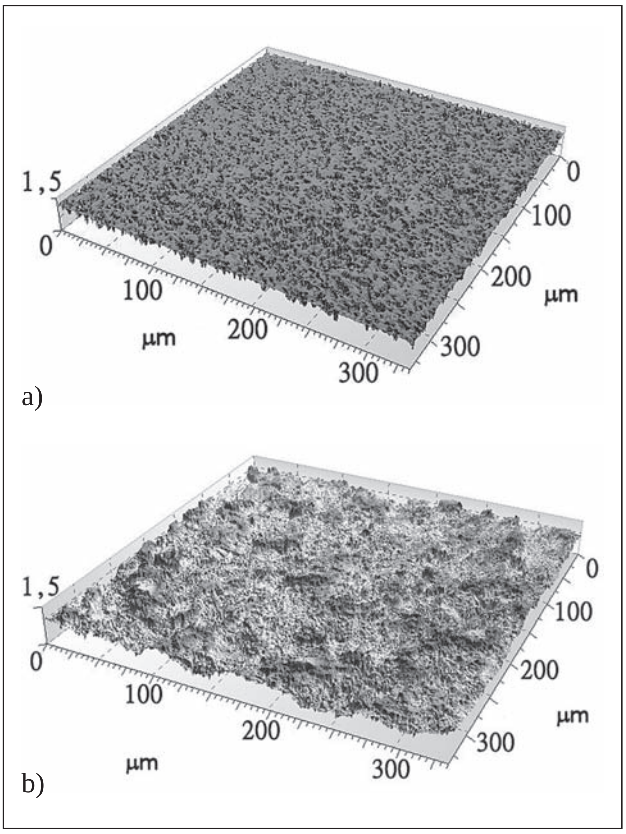


Figure 4 Optical test profilometer (CCI) image - '3-dimensional' presentations for: a) polished titanium; b) sandblasted and etched titanium

Table 2 **Surface texture parameters**

Material / parameter	Ti polished	Ti sandblasting and etching
S_a	0,067	0,72
S_p	0,104	7,441
S_q	0,426	1,988
S_v	1,29	11,201
S_z	1,172	18,642
S_{sk}	- 2,392	- 0,015
S_{ku}	10,037	3,618

Where:
S_a - arithmetic mean height, S_p - maximum peak height, S_q - root mean square height, S_v - maximum pit height, S_z - maximum height, S_{sk} - skewness, S_{ku} – kurtosis.

RESULTS AND DISCUSSION

Figures 2 and 3 show views of the topography of the surface of the samples illustrated scanning electron microscope at various magnifications for polished titanium (Figure 2) and sandblasted and etched (Fig. 3).

Microstructure, as shown in Figures 2 and 3 show marked differences in surface morphology. The sample after surgery sandblasting and etching (Figure 3) has a much more developed than the sample surface polished. Treatment of this type are in implants because the surface structure plays a critical role in the process of osseointegration.

Figures 4 and 5 show images of the surface topography, and schedules the ordinate with the curves and Table 2 lists the most important parameters of surface texture of tested samples.

A higher value of the average arithmetic deviation of surface roughness S_a, basic parameter amplitude for the quantitative assessment of the analyzed surface, was recorded for a sample of titanium after sanding and polishing. For the sample polished S_a parameter was more than 10 times lower than the sample after sandblasting and etching. A similar trend was observed for the mean deviation of surface roughness S_q. S_{sk} parameter of tested samples was negative, which indicated plateau shape of their surface.

Obtained high values of S_{ku} resulted from a large slenderness distribution curve ordinates. Higher values in excess of magnitude, the maximum height of elevation surface S_p, the maximum depth of the recess area S_v and the maximum height of the surface S_z were recorded for samples after sandblasting and etching. The histograms, shown in Figure 4, allowed to observe the distribution of individual points in the test profile. The vertical axis is a measure of the depth, and the horizontal axis is the percentage of the entire profile. In Figure 4 it is indicated Abbott-Firestone Curve - load curve which specifies for a given depth percentage of the material in relation to the present area.

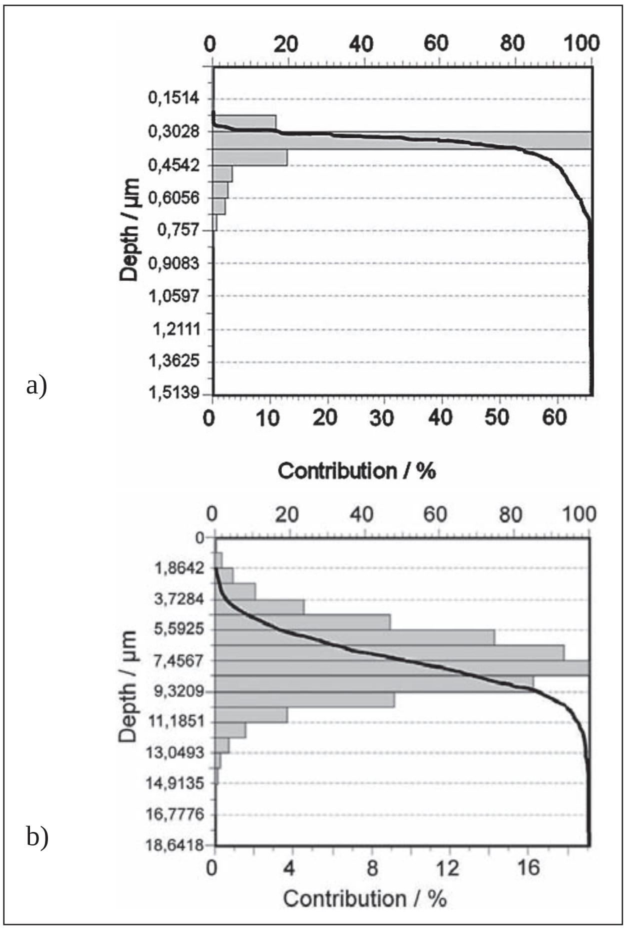


Figure 5 Depths histogram with Abbott-Firestone curves of titanium: a) polished and b) sandblasted and etched titanium

Table 3 **Results of hardness measurement**

Parameter	Mean	Standard deviation
Indentation hardness / H_{IT}	3,909 GPa	0,1
Vickers hardness / HV	362 HV	8,9
Elastic modulus / E	122,73GPa	8,5
Stiffness / S	494 mN/µm	9,8
Contact area / A	12,7 µm	2

In a next step hardness tests were performed using the nano-hardness tester using NHT2 Berkovich Indenter using the following parameters during one cycle: F = 50 mN, dF/dt = 100 mN / min, pause = 10,0 s. Young's modulus, stiffness, contact surface and hardness were calculated by the software on the device model Oliver-Pharr assuming a Poisson's ratio ν = 0,3. The tests were subjected to a sample of titanium polished. The measurement results are given in Table 3.

CONCLUSIONS

Titanium is next to austenitic steels and cobalt alloys an important group of metallic materials used in the manufacture of medical accessories, used among others in arthroplasty of the hip and knee joints and dental implant.

Depending on the work carried out in the mechanical and chemical treatments of titanium for medical applications a surface with varying degrees of expansion was achieved.

As a result of sandblasting and eching treatment the titanium structure has been transformed.

Through these treatments the structure a high degree of development of the surface roughness and greater has been obtained, which has a positive effect on obtaining a stable connection of the implant with the bone tissue.

Test of mechanical properties - nanohardness test showed a high hardness and Young's modulus of the tested samples.

REFERENCES

[1] D. Brunette, P. Tengvall, M. Textor, P. Thomson, Titanium in Medicine: Material Science, Surface Science, Engineering, Biological Responses and Medical Applications, Springer-Verlag, Berlin Heidelberg, 2001.

[2] M. Balazic, J. Kopac, Review: titanium and titanium alloy applications in medicine, International Journal of Nano and Biomaterials 1 (2007)1, 3-34.

[3] D. Williams (ed.). Definitions in biomaterials, Elsevier, Amsterdam-Oxford-New York-Tokyo, 1987.

[4] Madej M., Properties of tribological systems with diamond-like carbon coatings, Monography 46, Kielce, 2013.

[5] P. Ostman, M. Hellman, I. Wendelhag, L. Sennerby, Resonance Frequency Analysis Measurements of Implants at Placement Surgery, International Journal of Prosthodontics 19 (2006), 77-83.

[6] F. Likibi, M. Assad, P. Jarzem, M. Leroux, C. Coillard, G. Chabot, C. Rivard, Osseointegration study of porous nitinol versus titanium orthopaedic implants, European Journal of Orthopaedic Surgery and Traumatology 14 (2004), 209-213.

[7] R. Eason (ed.), Pulsed laser deposition of thin films: applications-lead growth of functional materials, Wiley, New York, 2007.

[8] M. Janiszewski M., G. Gałuszka, A. Ochwanowska, A. Gonciarz, A. Hak, P. Ochwanowski, R. Gałuszka, M. Oryniak, Analiza biomechaniczna dynamiki i statyki narządu ruchu u muzyków instrumentalistów, Medycyna Pracy 56 (2005)1, 25-33.

[9] S. Adamczak, J. Świderski, M. Wieczorowski, R. Majchrowski, T. Miller, A. Łętocha, Założenia do oceny wiarygodności pomiarów topografii powierzchni w różnych skalach, Mechanik 3 (2015), 81-87.

[10] M. Zeleňák, J. Valíček, S. Hloch, D. Kozak, I. Samardžić, M. Harničárová, J. Klich, P. Hlaváček, R. Cincio, Comparison of mechanical properties of surface layers with use of nanoindentation and microindentation tests, Metalurgija 51 (2012)3, 309-312.

Note: The responsible translator for English language is Przemysław Szczepańczyk, Kielce, Poland.