Acta of Bioengineering and Biomechanics
Vol. 18, No. 1, 2016

Original paper
DOI: 10.5277/ABB-00193-2014-02

Microstructural and micromechanical tests of titanium biomaterials intended for prosthetic reconstructions

ANNA M. RYNIEWICZ[1]*, ŁUKASZ BOJKO[1], WOJCIECH I. RYNIEWICZ[2]

[1] AGH University of Science and Technology, Faculty of Mechanical Engineering and Robotics, Kraków, Poland.
[2] Jagiellonian University Medical College, Faculty of Medicine, Department of Prosthetic Dentistry, Kraków, Poland.

Purpose: The aim of the present paper was a question of structural identification and evaluation of strength parameters of Titanium (Ticp – grade 2) and its alloy (Ti6Al4V) which are used to serve as a base for those permanent prosthetic supplements which are later manufactured employing CAD/CAM systems. *Methods*: Microstructural tests of Ticp and Ti6Al4V were conducted using an optical microscope as well as a scanning microscope. Hardness was measured with the Vickers method. Micromechanical properties of samples: microhardness and Young's modulus value, were measured with the Oliver and Pharr method. *Results*: Based on studies using optical microscopy it was observed that the Ticp from the milling technology had a single phase, granular microstructure. The Ti64 alloy had a two-phase, fine-grained microstructure with an acicular-lamellar character. The results of scanning tests show that titanium Ticp had a single phase structure. On its grain there was visible acicular martensite. The structure of the two phase Ti64 alloy consists of a β matrix as well as released α phase deposits in the shape of extended needles. Micromechanical tests demonstrated that the alloy of Ti64 in both methods showed twice as high the microhardness as Ticp. In studies of Young's modulus of Ti64 alloy DMLS technology have lower value than titanium milling technology. *Conclusions*: According to the results obtained, the following conclusion has been drawn: when strength aspect is discussed, the DMLS method is a preferred one in manufacturing load structures in dentistry and may be an alternate way for the CAD/CAM system used in decrement processing.

Key words: *CAD/CAM system, dental prosthetics, Direct Metal Laser Sintering (DMLS), microstructure, microhardness, titanium and titanium alloy*

1. Introduction

In the past few years, Computer Aided Design/ Computer Aided Manufacturing systems have become more often used in the process of making permanent prosthetic supplements. Most often, they are performed in three stages: scanning and representation of shape, design of supplement, processing by milling. However, there is an alternative method: Selective Laser Sintering (SLS) with a Direct Metal Laser Sintering (DMLS) [6], [8], [9], [21], [22] (Fig. 1). The method was developed by the Electro Optical Systems GmbH (EOS) based in Germany. Using this method, therapeutic structures can be made with the aid of CAD/CAM procedures. During the CAM stage, the metal base is manufactured during the process of laser beam sintering of titanium-aluminium-vanadium powder in all its layers. Details of the method are as follows: a layer of 0.02 mm thick powder is placed on a working platform of the device; next, laser beam of infrared characteristic is applied to the surface of powder according to a bitmap serving as a virtual pattern of the base being produced. Then, the working platform goes down and the next layer of powder is applied. The process of quick hardening after melting gives a homogenized structure of the material. After the process, excess of unused powder is ready for the next production cycle. This results in lower production costs and the amount of recycling material.

---

* Corresponding author: Anna M. Ryniewicz, Faculty of Mechanical Engineering and Robotics, AGH University of Science and Technology, Al. Mickiewicza 30, 30-059 Kraków, Poland. Phone number: 48 12 421 57 15, e-mail: anna@ryniewicz.pl

Received: September 30th, 2014
Accepted for publication: November 3rd, 2015

The following was the aim of the research work: structural identification and finding strength parameters of Titanium and its alloy used for making base elements of prosthetic structures by the CAD/CAM method – those which are produced by two different methods:

- milling preceded by heat and plastic treatment,
- laser increment sintering of selective metal powders.

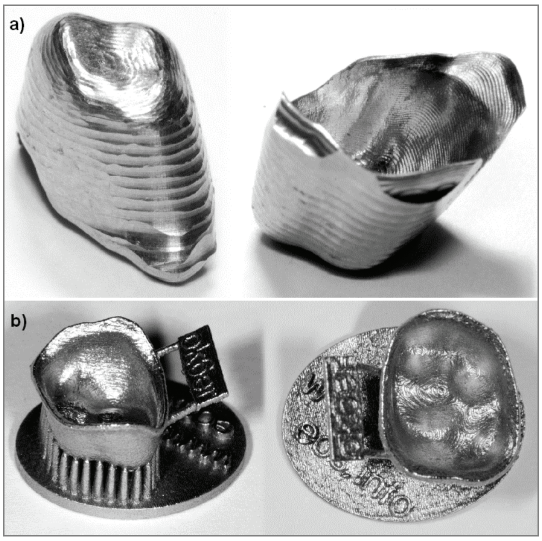

Fig. 1. Substructure of titanium crown:
(a) using subtractive manufacturing technology with milling,
(b) following additive laser sintering

2. Materials and methods

Samples of commercially pure Titanium – grade 2 and of Ti6Al4V alloy intended for making dentistry prosthetic structures by the CAD/CAM methods were the material used in the research study.

Analysed were samples of commercially pure titanium (Ticp) known as "Everest T Blank" (KaVo Dental GmbH, Biberach/Riss, Germany) which were treated using CAD/CAM procedure of the KaVo Everest system, as well as samples of Ti6Al4V alloy known as EOS Titanium 64 (Electro Optical System GmbH, München, Germany) – Ti64 manufactured by the DMLS method (Table 1). Rectangular prisms were formed of the said materials, both of 15 mm × 5 mm × 2 mm dimensions. The Ticp samples were cut from a factory-made, cylinder and block shapes; the Ti64 samples were cut-off after the process of increase sintering of selective powders in the EOSINT M 270 apparatus.

Table 1

Elt.	Conc.	
	Ticp – grade 2	Ti64
Titanium	balance	balance
Aluminum	–	5.5–6.75 wt.-%
Vanadium	–	3.5–4.5 wt.-%
Oxygen	<2500 ppm	<2000 ppm
Nitrogen	<300 ppm	<500 ppm
Carbon	<1000 ppm	<800 ppm
Hydrogen	<150 ppm	<150 ppm
Iron	<3000 ppm	<3000 ppm

Structural analyses were carried out on cut, polished and etched samples. With this aim in mind, the samples were imbedded in resin and polished using a Struers TegraForce-5 device, on which, with the aid of pre-programmed operations, the surface layers required for microstructural tests were obtained. In the next stage the samples were etched in a 10% HF solution with the following composition: 10 ml HNO_3 + 20 ml HF + 20 ml glycerine.

Microstructural tests of Ticp and Ti64 were conducted using an optical microscope from the company Nicon Eclipse ME 600 with digital image recording as well as a scanning microscope from the company JOEL JSM 5510LV coupled to a digital processing accessory (IXRF System 500 Digital Processing) for X-ray analysis. The accessory made it possible to determine the qualitative and quantitative chemical composition in micro-area at the marked points.

Hardness was measured with the Vickers method and Instron Wolpert TESTOR 2100 appliance. A diamond indenter was driven into each sample with the load of 1.961 N at a specified speed of load and relieve. Time of keeping the maximum load: 10 s. Based on the measurements of the diagonal imprints a Vickers hardness was determined. The testing was performed in accordance with a normalized procedure [13].

Micromechanic properties of samples: measurements of microhardness and Young's modulus value were done by a Micro Combi Tester made of CSEM Instruments. Here, a method of indenting a sample by diamond penetrator shaped as a regular pyramid of a square base was applied. Values of force and deepness of penetration were constantly measured, both during loading and unloading cycles. Maximum value of load was 200 mN, speed of load and unload: 400 mN/min, period of maximum load: 5 s. The module of positioning the samples, working with a 1 μm accuracy, made it possible to determine the point of inserting the indenter as well as random selection of its place. The accuracy of measurement of loading force of the indenter was 0.15 mN; the accuracy of measurement of deepness of penetration was 0.3 nm. For each cycle, relation of load of indenter/deepness of penetration was determined. Analysis of micromechanical properties was made with the use of the Oliver and Pharr method, according to which microhardness (HV) and module of elasticity of analysed material (E) were calculated from an indenting curve.

3. Results

3.1. Microscope analysis

The results of the titanium Ticp and Ti64 alloy tests conducted with a Nicon Eclipse ME 600 optical microscope took the form of microstructure images in different magnifications. The present study presents representative images of Ticp and Ti64 alloys in the same magnification (Fig. 2). Ticp made with milling technology was shown to possess a single-phase granular microstructure. The average sizes of grains in cross-sectional and longitudinal profiles were similar, i.e., 20 μm. The Ti64 alloy from laser sintering had a two-phase, fine-grained microstructure with an acicular-lamellar character. Tests carried out on both materials with an optical microscope revealed no discontinuities. The results of scanning tests on Ticp and Ti64 alloys included SEM images taken with a JOEL JSM 5510LV microscope as well as analyses of their chemical composition in microareas and at randomly selected points of these microareas using an EDS accessory. The sequence of Fig. 3 and Fig. 4 shows selected representative SEM images of the microstructure of Ticp and Ti64 samples. Titanium Ticp possesses a single-phase structure. The grains have similar sizes. Visible in the titanium grains is acicular martensite (Fig. 3). The structure of the two phase Ti64 alloy consists of a β matrix as well as released α phase deposits in the shape of extended needles (Fig. 4). The chemical composition of both biomaterials was analysed using an EDS accessory. The presence of titanium was identified in the micro-area of the Ticp surface. Three selected points were tested (Fig. 5).

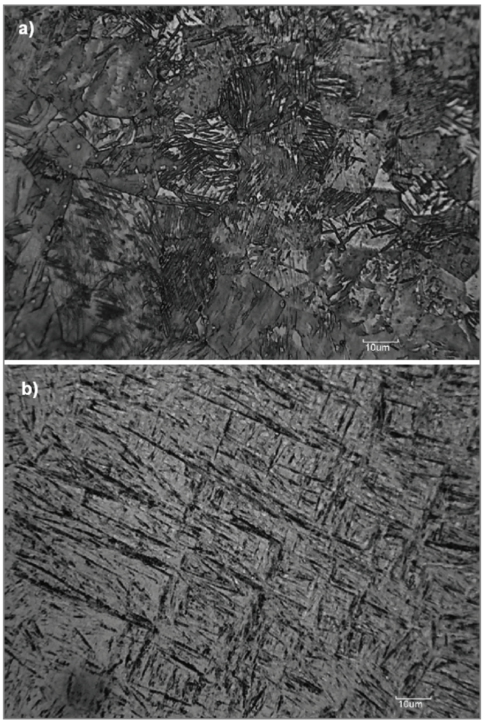

Fig. 2. Microstructure images from an optical microscope: (a) commercially pure titanium – grade 2, (b) Ti64 alloy

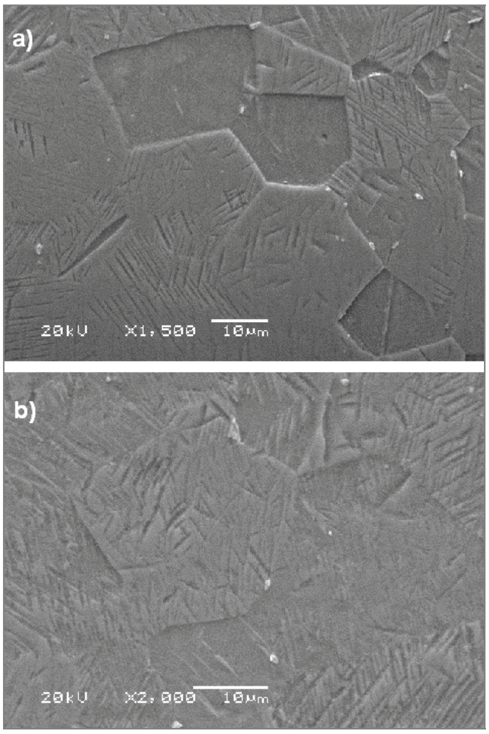

Fig. 3. SEM images of the microstructure of the Ticp sample – grade 2

A similar analysis was carried out for the Ti64 alloy. In this case, titanium, aluminium and vanadium were all identified on the surface tested. The composition of the elements in the selected micro-area is presented in Table 2. Points on the surface under study were also analysed. Point 1 constitutes phase α, while points 2 and 3 constitute phase β (Fig. 6). The chemical composition of particular points is presented in Table 3.

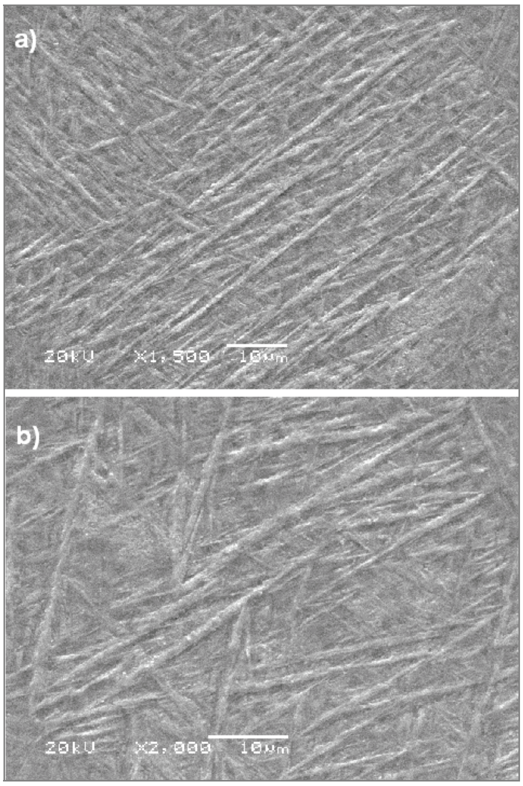

Fig. 4. SEM images of the microstructure of the Ti64 sample

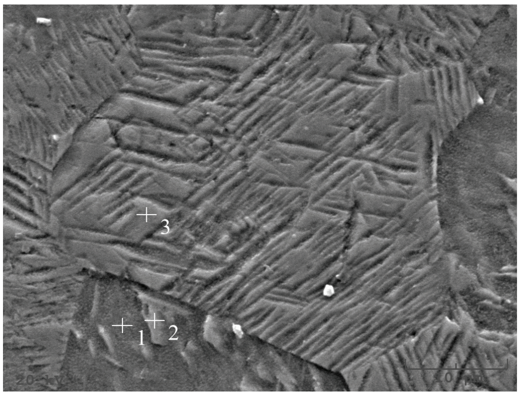

Fig. 5. SEM images of Ticp – grade 2 marked with points for analysing the chemical composition

Table 2. Chemical composition of a selected area on the surface of Ti64 sample

Elt.	Intensity (c/s)	Error 2-sig	Atomic %	Conc. (wt.%)
Aluminium	36.96	2.220	12.322	7.329
Titanium	494.31	8.118	85.323	90.027
Vanadium	13.26	1.330	2.355	2.644
			100.00	100.00

Table 3. Chemical composition of selected points on the surface of the Ti64 sample

Point	Elt.	Intensity (c/s)	Error 2-sig	Atomic %	Conc. (wt.%)
1	Aluminum	38.81	2.275	13.658	8.175
	Titanium	459.58	7.827	84.198	89.402
	Vanadium	11.38	1.232	2.144	2.423
				100.00	100.00
2	Aluminum	34.64	2.149	12.002	7.127
	Titanium	477.69	7.980	85.569	90.150
	Vanadium	13.18	1.326	2.429	2.723
				100.00	100.00
3	Aluminum	38.51	2.266	12.942	7.718
	Titanium	483.93	8.032	84.365	89.251
	Vanadium	15.02	1.415	2.693	3.032
				100.00	100.00

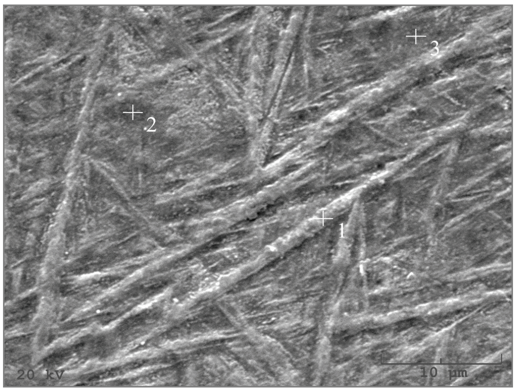

Fig. 6. SEM images of Ti64 alloy marked with points for analysing the chemical composition

3.2. Micromechanical analysis

Vickers hardness value was measured with the use of Instron Wolpert TESTOR 2100 device; it was determined as an average value of 30 trials. Table 4 shows results of measurements of hardness by Vickers method.

Table 4

No.	The test material	The average value of microhardness HV, MPa	The measurement uncertainty type A $u_{(H)}$, MPa
1	Ticp	2167.2	76.4
2	Ti-6Al-4V	4583.6	101.8

Results of micromechanic values: microhardness and Young’s modulus, were measured by MCT appliance as an average value of 30 measurements of each sample. Figure 7 shows examples of MCT indenting curves.

Table 5 presents results of micromechanic Oliver and Pharr tests.

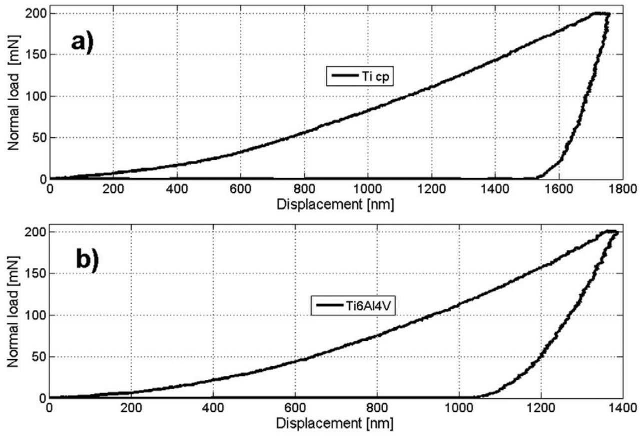

Fig. 7. Indenting curves of MCT tests:
(a) for the sample of Ticp for machining,
(b) for the sample Ti6Al4V DMLS technology

Table 5. Summary results of micromechanic Oliver and Pharr tests

No.	The test material	The average value of microhardness H, MPa	The measurement uncertainty	The average value of Young's modulus E, GPa	The measurement uncertainty
			$u_{(H)}$, MPa		$u_{(E)}$, GPa
1	Ticp	2275.1	78.5	136	4
2	Ti-6Al-4V	4485.2	98.2	130	5

Statistical evaluation of the study was determined by analysis of variance. The Shapiro–Wilk test examined the nature of the distribution of the measurement results according to the theory of Gauss. Dispersion of results was obtained by determination of measurement uncertainty. The standard uncertainty was calculated using a statistically defined variance [14].

4. Discussion

Microstructural tests of commercially pure titanium Ticp – grade 2 showed that the material possesses a uniform, grainy, single-phase structure, which is confirmed by the results of other authors [12]. The sizes of the grains were similar and amounted to 20 μm. The grains exhibited good mutual adhesion, growth and regularity of shape (Fig. 3). The observation revealed the presence of acicular martensite in the area of the grains, which probably developed during the heat treatment. The heat treatment process for the Ticp blanks is not known, since it is a trade secret of the producer. The chemical composition analysed in a selected micro-area and points confirmed that the material was commercially pure titanium (Fig. 5).

Microstructural tests carried out on the Ti64 alloy made with DMLS technology led to the conclusion that the material, composed of titanium, aluminium and vanadium, possesses a uniform two-phase construction, acicular-lamellar in form, and is composed of a β phase matrix and released α phase deposits that take the shape of needles oriented in different directions (Fig. 4). The two-phase Ti64 alloy includes the two most important elements stabilising phase α and phase β. Aluminium dissolves well in a permanent solution α, stabilises and strengthens phase α in a solution and also increases its strength. Simultaneously, it reduces the density of the alloy and increases the thermal stability of phase β. Vanadium, which is an isomorphic element, stabilises phase β and also helps reduce the allotropic transformation $Ti_{\alpha} \leftrightarrow Ti_{\beta}$. The microstructure of the Ti64 alloy is composed of a mixture of phases α and β. [1]. A similar profile of research for titanium alloys in medical applications was realized by Chlebus et al. [5]. Elemental analysis of the Ti64 alloy confirmed the presence of the following elements: titanium, aluminium and vanadium. An analysis at randomly selected points revealed no uneven percentage distribution of the alloy's metal constituents (Fig. 6, Table 3). The microstructure of the material following sintering shows a uniform chemical composition and a lack of porosity. The microstructure formed as a result of the sintering process is a problem that has occupied several authors [4], [7], [10], [11], [15], [20], [23], [24]. The lamellar microstructure of Ti64 alloy has been confirmed by Ramosoeu et al. [16] and Yadroitsev et al. [24]. The two-phase microstructure of Ti64 produced by laser sintering has also been identified by Rafi et al. [15] as well as Vranken et al. [23]. Using optical micrographs Rafi described the microstructure of Ti64 alloy, which is composed primarily of an α phase and a small amount of β within the prior β columnar grains oriented along the build direction. The α phase possesses a lamellar morphology with β surrounding the α lamellae boundary.

The substructures of crown- or bridge-type prosthetic reconstructions must have strength properties which ensure the transfer of occlusal loads, meet high fatigue limit conditions, be resistant to corrosion, have high density and a low Young's modulus, which guarantees optimal contact between the restoration and hard tissue of the SS [3]. These characteristics are determined by the microstructure of the biomaterials, from which fixed prosthetic reconstructions are made.

Tests on Ticp and Ti64 microstructures confirmed that the selectively sintered alloy would be the best of these biomaterials to use as a prosthetic substructure. It possesses a two-phase structure with a varying fine-grained orientation. Compared to the single phase granular structure of Ticp such a structure would provide greater strength and durability in prosthetic reconstructions, which must possess a thin wall and a step in the marginal gingiva (Fig. 1). Once the sintering process is complete, the unconsumed powder can be used in the next production cycle. This reduces the production costs and minimises the waste recycling process compared with milling technology.

Based on the examination performed with the use of Vickers method as well as of Oliver and Pharr method, it can be stated that Ti6Al4V titanium revealed above twice as high microhardness as Ticp measured by both methods. Young's modulus of longitudinal elasticity coefficient for Titanium alloy derived from DMLS technology was lower than Young's modulus of Titanium derived from heat and plastic working intended for decrement working by milling in the KaVo Everest system. This may serve as indication and support for DMLS technology to be used for making supports of prosthetic constructions. Due to the similarity of value of elasticity modulus of the material and modulus of elasticity of human hard tissue, better transmission of contact loads from therapeutic structure to the hard tissue of stomatognathic system can be achieved [2], [12], [17]–[19].

In the second half of the 19th century, G.H. Meyer, C. Cuman, and J.D. Wolff found out that the structure of the bone and its growth direction are determined by the current state of stress. Experimental verification of selected mechanical stimulators of bone tissue remodeling is presented in the work of T.D. Brown et al. (1990). The authors on the basis of their tests demonstrated that the parameters which influenced the bone tissue remodeling include density of distortion energy, the maximum principal stress and strain and longitudinal shear stress. In conditions of occlusion and chewing conditions, there occur stress and strain in stomatognathic system, which constitute stimulators of bone tissue remodeling. As a result of improper construction solution (shape, lack of smooth transitions, errors of execution and rear, the material being too rigid) excessive stress concentration under constantly repeated and variable occlusal loads, especially in the region of the degree, can result in prosthetic treatment failure. Such a phenomenon does stimulate physiological processes on hard tissue, which cooperates with the therapeutic construction. When stiffness criteria are discussed and compared with those of bones and teeth, it seems that Ti6Al4V alloy derived from DMLS technology is better than pure Titanium. Further it does not require decrement working during which vibrations are present as well as use up of milling cutters which, as a consequence, may result in inaccurate make of the prosthetic construction.

5. Conclusions

Biomaterial tests on the Ticp and Ti64 alloy using optical and scanning microscopy confirmed a uniform, single-phase granular microstructure of titanium intended for milling in the KaVo Everest system and a uniform two-phase fine-grained structure of the Ti64 alloy produced through the additive technique of selective direct metal laser sintering.

When measuring microhardness, essential differences can be noted between samples made of technically pure Titanium and intended for loss treatment and those of Ti6Al4V alloy derived from sintering process. The Titanium alloy has its microhardness about two times greater and its value of Young's modulus is lower. Young's modulus for Titanium alloy is lower than technically pure Titanium used in the KaVo Everest system.

The tests showed that the additive technique of selective direct metal laser sintering, which produces a substructure made from Ti64 alloy, is the new preferred technology (in terms of biomaterial structure) for making load-bearing structures for dentistry. It can serve as an alternative to traditional methods based on traditional casting as well as milling-based CAD/CAM methods. This technology does not lead to a loss of material typical of milling procedures and it is pro-ecological.

Acknowledgement

This work was supported by the grant No. 15.11.130.967 of AGH The University of Science and Technology and a research project 410/UPB/WL No. 2013/K/ZDS/003896 of Jagiellonian University Medical College, Poland.

References

[1] BARRIOBERO-VILA P., *Effect of heat treatments on the microstructure of deformed Ti-6Al-4V*, Wien, 2010.

[2] BĘDZIŃSKI R., *Experimental and numerical methods in biomechanics*, Biocybernetics & Biomedical Engineering, 2007, 27(1/2), 275–292.

[3] BURNAT B., WALKOWIAK-PRZYBYŁO M., BŁASZCZYK T., KLIMEK L., *Corrosion behaviour of polished and sandblasted titanium alloys in PBS solution*, Acta Bioeng. Biomech., 2013, 15(1), DOI: 10.5277/abb130111

[4] CHAHINE G., KOIKE M., OKABE T., SMITH P., KOVACEVIC R., *The Design and Production of Ti-6Al-4V ELI*, Customized Dental Implants, JOM, 2008, 60, 50–55.

[5] CHLEBUS E., KUŹNICKA B., KURZYNOWSKI T., DYBAŁA B., *Microstructure and mechanical behaviour of Ti-6al.-7Nb alloy produced by selective laser melting*, Materials Characterization, 2011, 62(5), DOI: 10.1016/j.matchar.2011.03.006

[6] CIOCCA L., FANTINI M., DE CRESCENZIO F., CORINALDESI G., SCOTTI R., *Direct metal laser sintering (DMLS) of a customized titanium mesh for prosthetically guided bone regeneration of atrophic maxillary arches*, Med. Biol. Eng. Comput., 2011, 49(11), 1347–52.

[7] DAS M., BHATTACHARY K., DITTRICK S.A., MANDAL C., BALLA V.K., SAMPATH KUMAR T.S. et al., *In situ synthesized TiB-TiN reinforced Ti6Al4V alloy composite coatings: Microstructure, tribological and in-vitro biocompatibility*, Journal of the Mechanical Behavior of Biomedical Materials, 2014, 29, 259–271.

[8] ISERI U., OZKURT Z., KAZAZOGLU E., *Shear bond strengths of veneering porcelain to cast, machined and laser-sintered titanium*, Dent. Mater. J., 2011, 30(3), 274–80.

[9] MANGANO C., PIATTELLI A., RASPANTI M., MANGANO F., CASSONI A., IEZZI G., SHIBLI J.A., *Scanning electron microscopy (SEM) and X-ray dispersive spectrometry evaluation of direct laser metal sintering surface and human bone interface: a case series*, Lasers Med. Sci., 2011, 26(1), 133–138.

[10] MURR L.E., ESQUIVEL E.V., QUINONES S.A., GAYTAN S.M., LOPEZ M.I., MARTINEZ E.Y. et al., *Microstructures and Mechanical Properties of Electron Beam- Rapid Manufactured Ti-6Al-4V Biomedical Prototypes Compared to Wrought Ti-6Al-4V*, Mater. Charact., 2009, 60, 96–109.

[11] MURR L.E., QUINONES S.A., GAYTAN S.M., LOPEZ M.I., RODELA A., MARTINEZ E.Y. et al., *Microstructure and mechanical behavior of Ti-6Al-4V produced by rapid-layer manufacturing, for biomedical applications*, Journal of the Mechanical Behavior of Biomedical Materials, 2009, 2, 20–32.

[12] ÖZCAN M., HAMMERLE C.H., *Titanium as a Reconstruction and Implant Material in Dentistry: Advantages and Pitfalls*, Materials, 2012, 5, 1528–1545.

[13] PN-EN ISO 6507-1:2007: *Metals – Vickers hardness test* – Part 1: *Test method.*

[14] Przewodnik PKN-ISO/IEC Guide 99, Wydawnictwo PKN, Warszawa 2010.

[15] RAFI H.K., KARTHIK N.V., GONG H., STARR T.L. STUCKER B.E., *Microstructures and Mechanical Properties of Ti6Al4V Parts Fabricated by Selective Laser Melting and Electron Beam Melting*, Journal of Materials Engineering and Performance, 2013, 22, 3872–3883.

[16] RAMOSOEU M.E., CHIKWANDA H.K., BOLOKANG A.S., BOOYSEN G., NGONDA T.N., *Additive manufacturing: characterization of TI-6AI-4V alloy intended for biomedical application*, Southern African Institute of Mining and Metallurgy advanced metals initiative: Light Metals Conference, Misty Hills, Muldersdrift, 27–29 October 2010, 337–344.

[17] RYNIEWICZ A., BOJKO Ł., RYNIEWICZ W., *Selected Mechanical Properties of Titanium in Dental Implantology Reconstruction Procedure*, Engineering of Biomaterials, 2012, 112, 48–53.

[18] RYNIEWICZ A.M., RYNIEWICZ W., *Strength tests and tribological properties of titanium intended for construction of permanent prosthetic restorations*, Implant Prosthetics, 2008, 1(30), 42–47.

[19] RYNIEWICZ A., RYNIEWICZ W., *The Estimation of Selected Properties of Titanium to Performance of Prosthetic Restorations in CAD/CAM*, Polish Journal of Enviromental Studies, 2007, 16(6C), 348–353.

[20] SONG B., DONG S., ZHANG B., LIAO H., CODDET C., *Effects of processing parameters on microstructure and mechanical property of selective laser melted Ti6Al4V*, Mater. Design, 2012, 35, 120–125.

[21] SZYMCZYK P., JUNKA A., ZIÓŁKOWSKI G., SMUTNICKA D., BARTOSZEWICZ M., CHLEBUS E., *The ability of S. aureus to form biofilm on the Ti-6Al-7Nb scaffolds produced by Selective Laser Melting and subjected to the different types of surface modifications*, Acta Bioeng. Biomech., 2013, 15(1). DOI: 10.5277/abb130109

[22] TRAINI T., MANGANO C., SAMMONS R.L, MANGANO F., MACCHI A., PIATTELLI A., *Direct laser metal sintering as a new approach to fabrication of an isoelastic functionally graded material for manufacture of porous titanium dental implants*, Dent. Mater., 2008, 24(11), 1525–1533.

[23] VRANCKEN B., THIJS L., KRUTH J.P., VAN HUMBEECK J., *Heat treatment of Ti6Al4V produced by Selective Laser Melting: Microstructure and mechanical properties*, Journal of Alloys and Compounds, 2012, 541, 177–185.

[24] YADROITSEV I., KRAKHMALEV P., YADROITSAVA I., *Selective laser melting of Ti6Al4V alloy for biomedical applications: Temperature monitoring and microstructural evolution*, Journal of Alloys and Compounds, 2012, 583, 404–409.