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## **THE INFLUENCE OF LASER ALLOYING OF Ti13Nb13Zr ON SURFACE TOPOGRAPHY AND PROPERTIES**

### **ABSTRACT**

The laser alloying is a continually developing surface treatment because of its significant and specific structuration of a surface. In particular, it is applied for Ti alloys, being now the most essential biomaterials' group for load-bearing implants. The present research was performed on the Ti13Nb13Zr alloy subject to laser modification in order to determine the treatment effects on surface topography and its some mechanical properties like nanohardness, Young's modulus, roughness. A pulse laser Nd:YAG was applied at three different laser pulse regimes: either 700 W, 1000 W or 1000 W treatment followed by 700 W modification at a pulse duration of 1 ms. The surface topography and morphology were examined using light microscopy and scanning electron microscopy with spectroscopy of X-ray energy dispersion. The mechanical properties were determined by nanoindentation tests and surface roughness with a use of profilograph. The wettability was tested with a goniometer. The obtained results demonstrate complex behavior of the material surface: decrease in penetration distance and increase in hardness after first laser treatment, maintenance of this trend when machining using a higher laser pulse power, followed by an increase in penetration and decrease in hardness after additional laser treatment at lower power input, due to which a surface with fewer defects is obtained. The change in Young's modulus follows the change in other mechanical properties, but not a change in roughness. Therefore, the observed hardening with the increase of the laser pulse power and then a small softening with the use of additional treatment with lower power can be attributed to some processes of remelting, diffusion and crystallization, sensitive to the previous surface state and heat energy flux. Despite that, the laser treatment always caused a significant hardening of the surface layer.

*Keywords: Ti13Nb13Zr alloy; laser alloying; nanoindentation; surface layer*

### **INTRODUCTION**

High requirements expected from medical implants, especially those used in orthopedics and dentistry, have led to increased research on modern biomaterials. In order to overcome the disadvantages of a single-phase implant i.e. low biocompatibility of metals and insufficient mechanical properties of ceramic materials, efforts have been made to develop appropriate modifications of metallic materials for medical implants [1].

Titanium and its technical-grade D and E alloys i.e. Ti6Al4V, Ti6Al7Nb and Ti13Nb13Zr have been used in tissue engineering. However, alloys with aluminum and/or vanadium possess some disadvantages, such as modulus of elasticity distinctly different in comparison to that of bone tissue, and the addition of V and/or Al causing adverse allergic reactions, neurogenic disorders, and increasing osteoporotic phenomena (adverse effects for softening bones), a disorder of the functionality, and that following, activity of many enzymes and neurotransmitters and damage to nerve cells may even initiate Alzheimer's disease [2-5]. Titanium alloy with zirconium and niobium shows no negative impact on the environment of human body. It causes the  $ZrO_2$  and  $Nb_2O_5$  oxides to stand neutral to the human body and improves the passive properties of the alloy. Also, the Ti13Nb13Zr alloy is characterized by better strength properties, the ability to osseointegrate and has the value of Young's modulus similar to the tissue of longitudinal bones. The properties of here tested Ti13Nb13Zr alloy have been already determined [2] as tensile strength 1030 MPa, yield strength 900 MPa, elongation ~15%, Young's modulus 79 GPa, fatigue strength 500 MPa at  $10^7$  cycles.

In order to improve the properties of titanium alloys used in medical engineering, many different surface modification techniques are used: plating [6], nanooxidation [7], ion implantation [8], anodizing [9], polishing [10], nitriding [11], nanopatterning [12], coating with diamond derivatives [13] or hydroxyapatite deposition [14-17]. Modern laser technologies such as hardening, melting, welding, alloying and ablation become also more and more used methods of modifying various materials by contemporary researchers [18]. The increase in interest in these methods is related to the possibility of local processing, satisfactory process efficiency, no deformation of the workpiece, lower cost, broad possibilities of material structure modification and the ability to automate the process and its control. Different structures are obtained far from equilibrium state, at laser machining during single milliseconds, thanks to the concentration of high power densities on the treated area. The result of their creation are i.e. improvement of mechanical and often anticorrosive properties or increase in hardness. However, this is usually obtained at the expense of surface quality [19, 20].

Titanium and its alloys are the subject of many studies using laser processing. In [21], scientists made a laser coating on the surface of titanium alloy and examined the microstructure, some mechanical properties and the corrosion resistance of the surface before and after laser treatment. In [22] the laser beam temperature distribution with single and multiple impulse on the surface of Ti6Al4V titanium alloy was studied. The formation of self-assembled nanostructures under the irradiation of a single-beam femtosecond laser was demonstrated for the surface of titanium [23]. The subject of another research [24] was an analysis of the operation of the ultra-short laser pulse titanium alloy. Surface properties with various laser processing parameters were also examined here. In [25], a titanium carbide ablation on the titanium surface was produced increasing the corrosion resistance of the titanium. The increase of titanium properties and refinement of its grain (obtaining a continuous layer consisting of plate grains) in the process of direct laser interference lithography was described in [26]. Other attempts were made [27-29] to change mechanical properties (tensile strength, elongation, stress properties) and Ti6Al4V alloy microstructure by selective laser melting process. Surface morphology of Ti6Al4V alloy with single-layer microparticles was observed to depend on the energy of a single micro-second laser pulse [30]. In [31], the chemical and morphological effects of the millisecond pulse of the Nd:YAG and  $CO_2$  laser in the titanium laser texturing process designed for bioengineering were

described. The control of the Nd:YAG laser welding parameters to avoid significant breaks unavoidable in the conventional titanium welding process was achieved [32]. Finally, fatigue strength, tensile strength and hardness, and surface topography of Ti13Nb13Zr alloy after selective laser melting were improved [33].

The present study aims to assess the impact of laser modification using the Nd:YAG laser with suitably selected parameters on the quality of the surface layer of the tested Ti13Nb13Zr alloy. Based on preliminary studies, three laser processing processes with different technological parameters have been carried out, which will allow to compare the impact of parameters on the microstructure and some mechanical properties of the top layer of the tested alloy. These tests are exploratory before planned further research on an increase in mechanical properties of this alloy by laser modification with the use of some nanomaterials.

## MATERIALS AND METHODS

The Ti13Nb13Zr alloy (about the chemical composition shown in Table 1) was tested. The samples constitute a quarter section of a 4 mm patch made of a rod with a diameter of 40 mm, cut out with a cutter.

**Table 1.** Chemical composition of the Ti13Nb13Zr alloy according to the producer's attestation, wt. %

Element	C	Fe	N	O	Zr	Nb	H	S	Ti
Ti13Nb13Zr	0.035	0.085	0.019	0.078	13.49	13.18	0.055	<0.001	rest

In order to adapt the substrate to the appropriate roughness and to get rid of scratches after cutting, other irregularities and impurities, the samples were sanded using abrasive paper grades: 220, 400 and 800. Grinding was performed by wet method on a double-disc hand-operated metallographic grinder and polisher (Saphir 330, ATM GmbH, Germany). After the process, the samples were thoroughly washed and dried with compressed air.

The samples prepared in this way, besides one being the reference material (MR), were then laser processed using the Nd:YAG pulse laser (TruLaser Station 5004, TRUMPF) at the parameters shown in Table 2. They were selected at by reconnaissance tests, in which as well a minimum number of surface layer defects and the best solution to the problem of oxidation of the material were determined. The use of double treatment in the same area was motivated by the observation of fewer cracks on the surface of the samples when applying an individual processes. The laser treatment was carried out under a shielding gas - argon. For the correct course of the melting process of the substrate, it was necessary to use protective gas with an argon content of not less than 99.987%.

The microstructure of the surface of MR and other samples after laser treatment was observed by light microscopy (UC50, Olympus) and scanning electron microscopy (JSM-7800F, JEOL, Japan). The chemical composition of the surface was examined using the same scanning electron microscope additionally equipped with an X-ray energy dispersion spectrometer (Octane Elite 25, EDAX Ametek, USA).

**Table 2.** Parameters of laser processing of the tested material

Sample	Power of the laser pulse [W]	Duration of the laser pulse [ms]	Frequency [Hz]	Energy [J]	Average power [W]	Linear speed [mm/s]
L1	700	1	25	0.7	17.55	1
L2	1000			1	25.05	
L2 + L1	1000+700			1+0.7	25.05+17.55	

Nanoindentation studies were carried out for MR and after laser treatment using a nanoindenter (NanoTest Vantage, Micro Materials, UK) equipped with a diamond three-sided Berkovich's indenter with an apical angle of 124.4°. A total of 25 measurements (5 x 5) were made. The indentations were spaced 25 µm apart. The indentation parameters are shown in Table 3.

**Table 3.** Parameters of nanoindentation

Parameter	Value
Maximum force [mN]	50
Time of force increase from the zero value [s]	20
Dwell time of maximum load [s]	10
Unloading time [s]	20

Hysteresis curves of load-strain were recorded during the test. Determination of instrumented Young's modulus ( $E_{IT}$ ), reduced Young's modulus ( $E_r$ ) and instrumented nanohardness ( $H_{IT}$ ) was possible thanks to the Olivier-Pharr method [34, 35] using the NanoTest results' analysis program.

The roughness of the samples before and after the laser modification was measured on a profilograph (Hommel Etamic Waveline T8000R, JENOPTIK, Germany) at a stretch of 4.5 mm. In each study, the arithmetic means of the deviations of the profile from the centerline - the Ra parameter, were calculated.

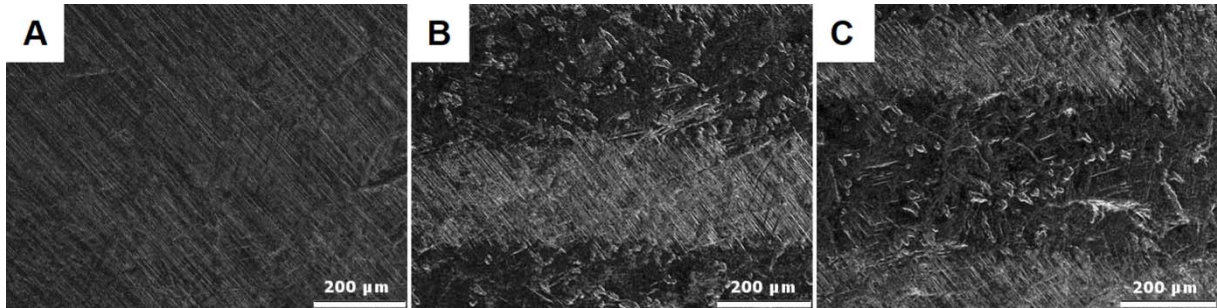
The water wettability angle after 10 seconds was measured for samples before and after laser treatment using an angular contact goniometer with a computer set (Attension Theta Lite, Biolin Scientific, Sweden) at room temperature. For each sample, three measurements were made using the falling drop method and the means were calculated.

## RESULTS AND DISCUSSION

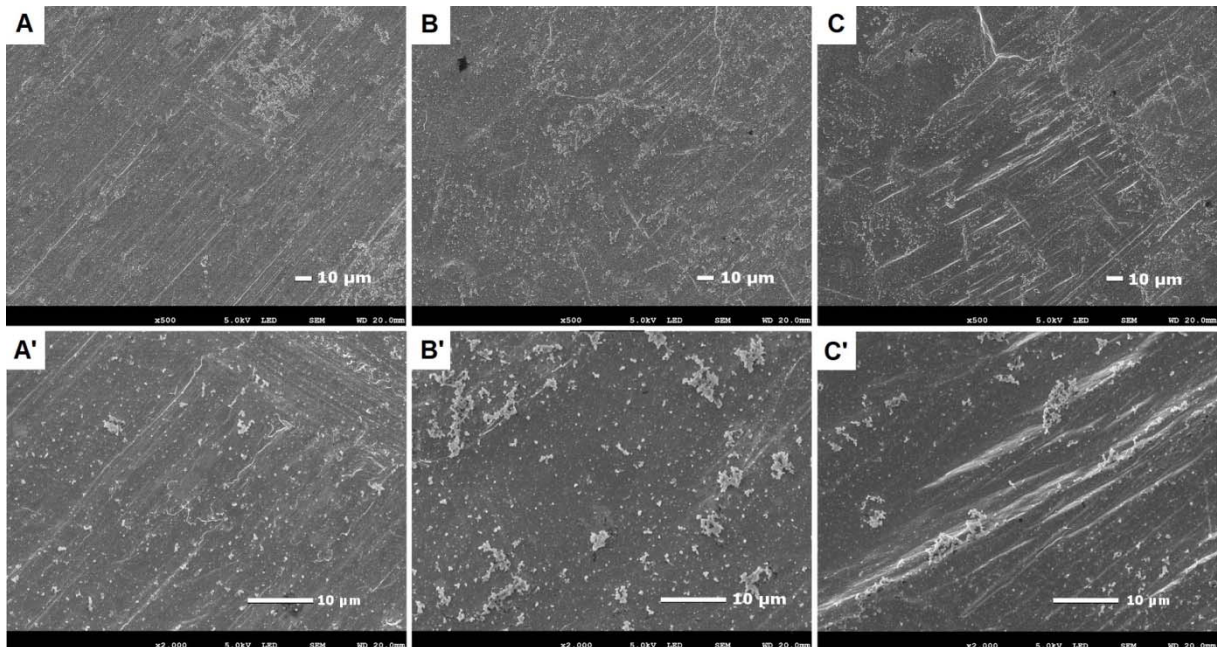
Figures 1 and 2 show the images of Ti13Nb13Zr alloy microstructure after grinding and laser treatment obtained by light and SEM microscopy. These images confirm the presence of laser modified surface layer on the substrate.

The microstructure of the surface of the L1 sample does not have visible laser tracks (Fig. 1.A), noticeable at low magnification, it is bright and uniform. One can see traces remaining after abrasive machining. It may indicate a slight modification of the laser surface layer. With the increase of the laser power the path becomes more visible under the light microscope, and

with the double treatment L2 + L1 is noticeable very clearly as dark stripes (Fig. 1.C). Despite overlapping of the paths in 50%, unevenness in the surface treatment is noticed.



**Fig. 1.** Surface microstructure observed under optical microscope: A - L1 laser treatment, B - L2 laser treatment and C - L2 + L1 laser treatment

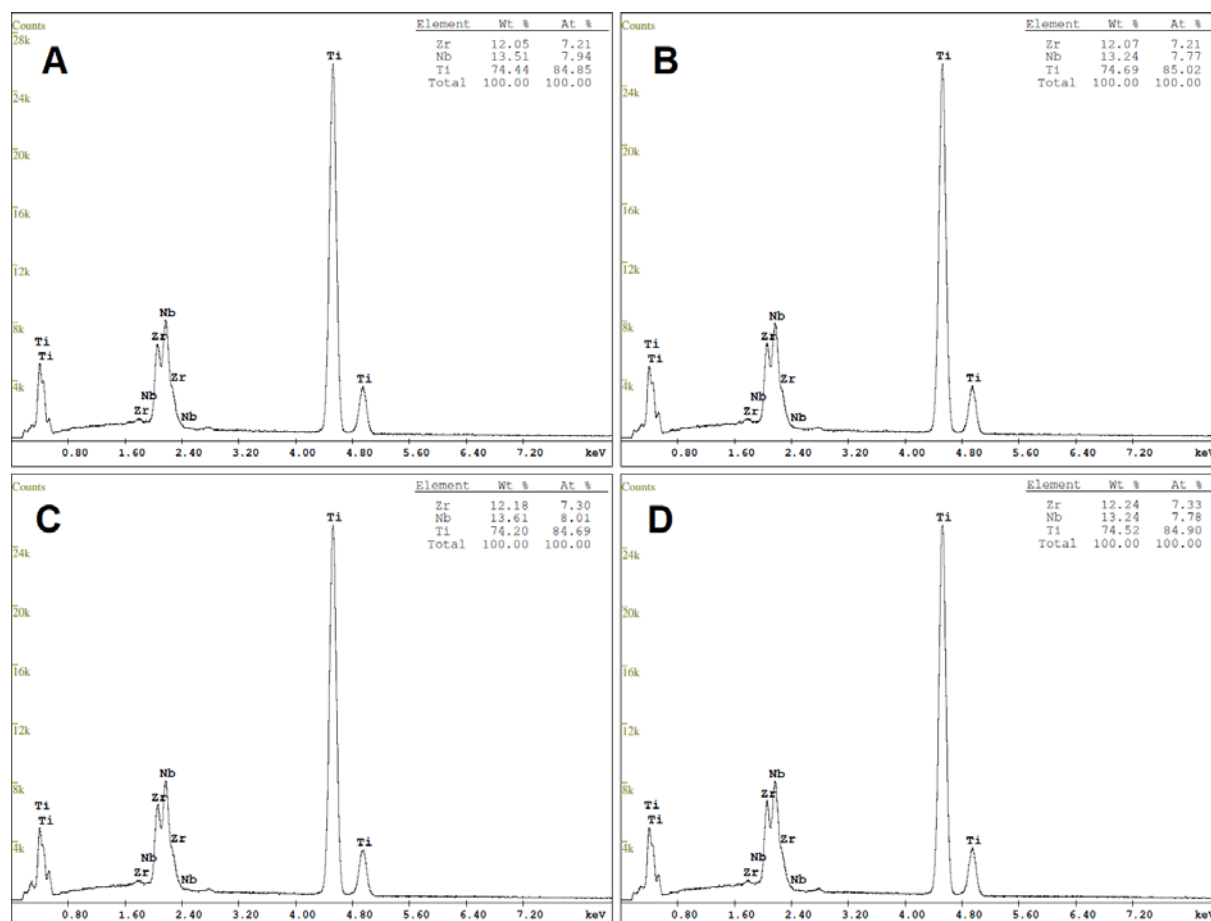


**Fig. 2.** Surface microstructure observed under SEM: L1 laser treatment A - 500x, A' - 2000x; L2 laser treatment B - 500x, B' - 2000x and L2 + L1 laser treatment C - 500x, C' - 2000x

SEM images should provide more detailed information on the changes occurring in the microstructure of the surface layer Ti13Nb13Zr alloy. Observation of the surface condition of the tested material after laser treatment did not show visible differences dependent on the selected process parameters.

The effects of laser treatment are visible in the form of cracks, chips and scratches that significantly affect the quality of the surface. The use of the L2 + L1 double treatment process (Fig. 2.C-C') allowed to reduce the number of defects, especially spatter and cracks in the surface layer, and allowed for a noticeable, more accurate penetration (no visible effects of abrasive machining).

The EDS analysis (Fig. 3.) did not show any significant changes in the chemical composition of the laser modified surface layer Ti13Nb13Zr alloy. The mass percentage values of individual alloying elements for MR and after treatment with different laser pulse powers are within the standard deviation.



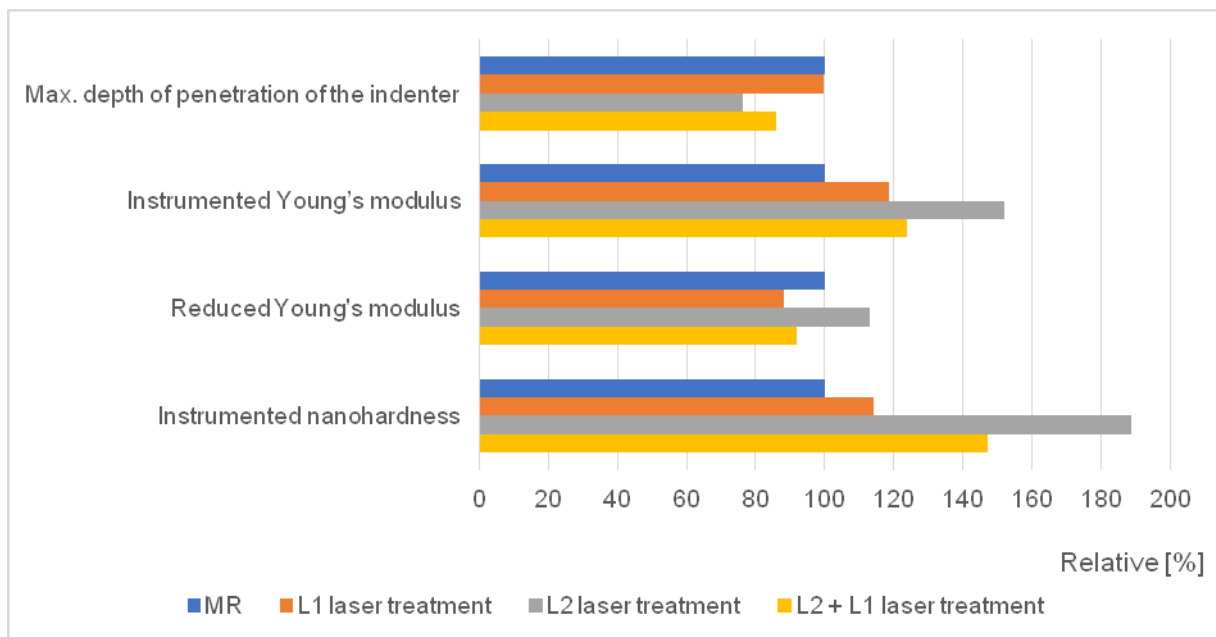
**Fig. 3.** EDS spectra and chemical composition analysis for: A - MR, B - L1 laser treatment, C - L2 laser treatment, D - L2 + L1 laser treatment

Nanoindentation research carried out allowed to register and develop the so-called load-strain diagrams, or curves of dependence of the indentation penetration depth from the given force. The graph for the native material (MR) was shown previously [36]. Three successive stages of nanoindentation are observed: an increase in the load from the indenter interface to the surface of the sample to reach the maximum value (along with increasing penetration depth), indentation in this position (stabilization of maximum depth) and unloading.

The comparison of results of obtained in nanoindentation tests for laser modified surfaces is shown in Fig. 4. It is observed that the applied L1, L2 and L2 + L1 laser treatment significantly influence the values of instrumented nanohardness, instrumented Young's modulus and reduced Young's modulus as compared to MR. The values of the mechanical properties increased with the applied increase of the laser pulse power parameter: hardness for L1 - about 15% about the reference sample and about 90% using the L2 laser treatment, instrumented Young's modulus, successively, by about 19% and about 52%. Using a lower

power treatment following a higher laser pulse power (L2 + L1 laser treatment), a slight softening (about 22% relative to L2) of the material is observed, which may be the result of some processes of melting, diffusion and recrystallization sensitive to the previous surface condition and thermal energy flux.

The increase in the laser pulse power also influences the maximum depth of penetration of the nanoindenter into the tested surface of the Ti13Nb13Zr alloy. The L2 sample showed a much lower maximum penetration depth of the indenter and better uniformity of distribution. This fact is related to obtaining by the sample the highest nanohardness and value of the Young's modulus. It can be concluded, therefore, that with the increase in the values of these mechanical properties, the depth of penetration of the indenter into the material decreases.

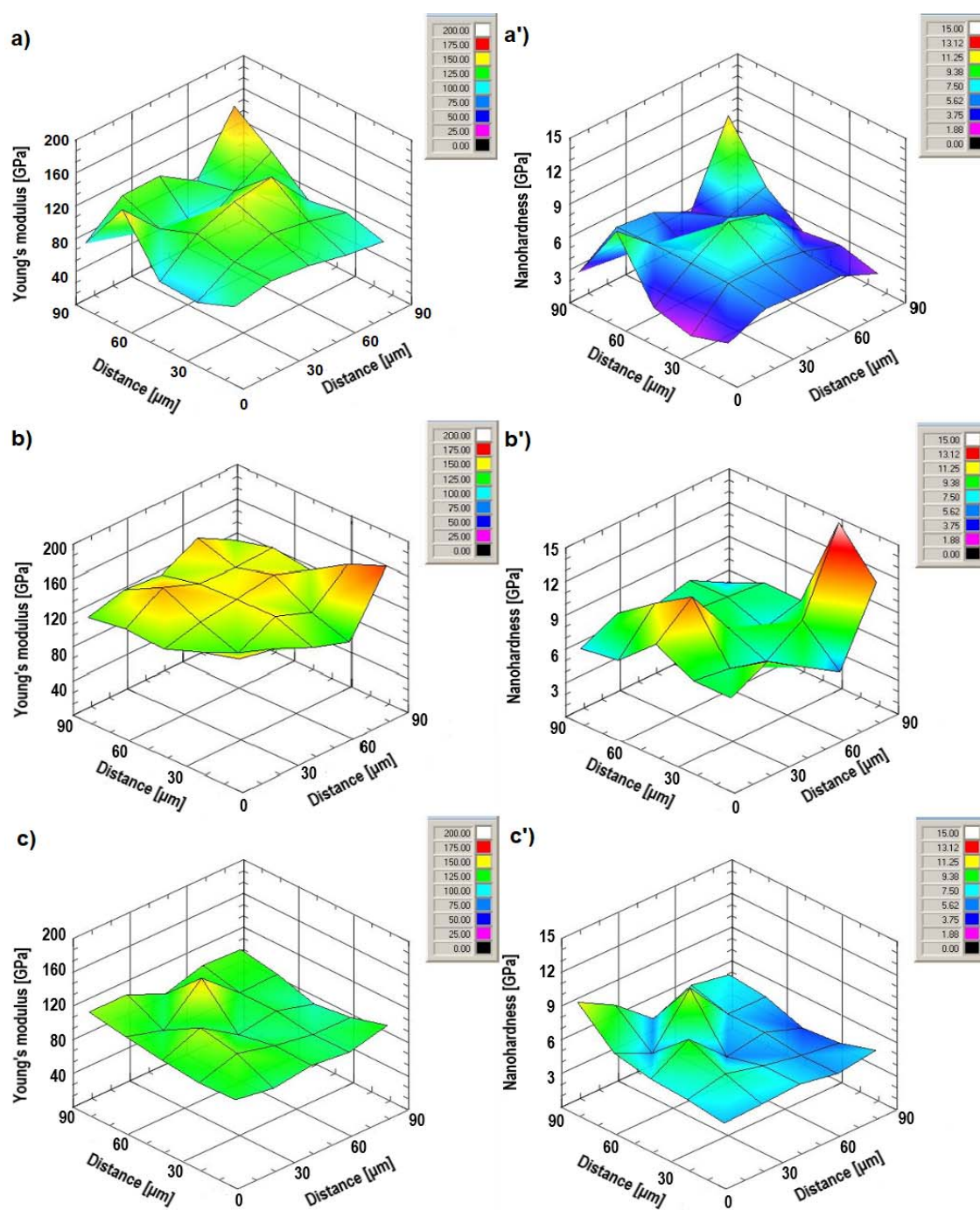


**Fig. 4.** Relation of laser treatment effects on the mechanical properties of the tested alloy

After nanoindentation, in order to better visualize the tested mechanical properties, 3D distributions of instrumented nanohardness and reduced Young's modulus were determined for laser treated samples L1, L2 and L2 + L1. They are shown in Fig. 5.

In the case of using laser treatment of Ti13Nb13Zr alloy, it can be observed that increasing the laser pulse power (or performing a double surface modification) leads to the equalization of the 3D distribution of the reduced elastic modulus and nanohardness within the surface.

Table 4 shows the roughness test results ( $R_a$ ) for Ti13Nb13Zr alloy samples before and after laser treatment. Figure 6 presents profiles of roughness before and after laser treatment of the material.



**Fig. 5.** 3D distribution of reduced Young's modulus: a) L1, b) L2, c) L2 + L1 and instrumented nano-hardness: a') L1, b') L2, c') L2 + L1

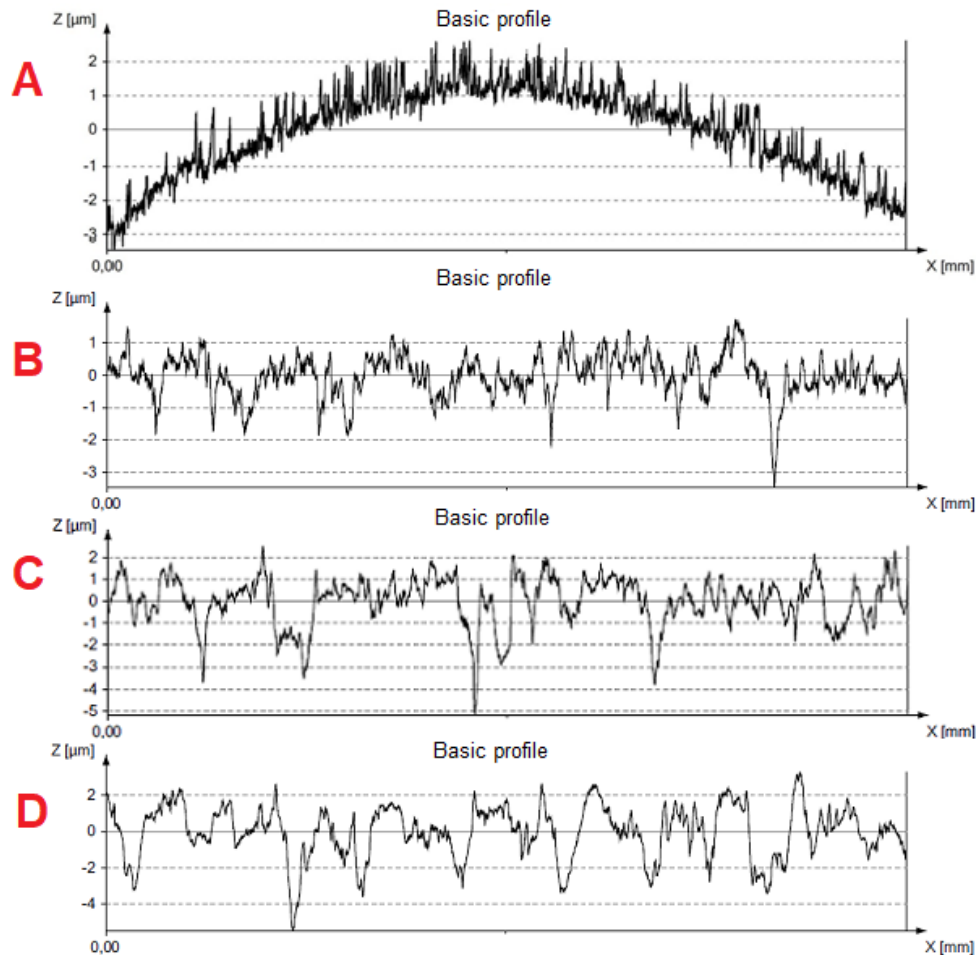
**Table 4.** The average arithmetic deviation of the profile from the mean line for Ti13Nb3Zr alloy

Sample	Roughness (Ra) [ $\mu\text{m}$ ]	Relative roughness [%]
MR	0.27	100
L1	0.46	170
L2	0.73	270
L2 + L1	1.10	407





The most massive increase in surface roughness compared to MR was observed for the sample with double laser modification L2 + L1. Based on these results, it can be concluded that an increase in laser pulse power (here the use of double modification) leads to an increase in the Ra roughness parameter value relative to the native material after abrasive machining.



**Fig. 6.** Roughness profiles for: A - MR, B - L1, C - L2, D - L2 + L1

Fig. 7 shows the angle of water wettability of the MR surface layer and samples after laser treatment with different parameters. The wettability decreases with increasing laser pulse power from  $87^\circ$  for MR to  $75^\circ$  for L2 laser treatment and  $74^\circ$  for the double modification process L2 + L1. These values indicate the hydrophilicity of this material and may be related to change in the surface roughness after laser treatment. As the wettability angle decreases, biological properties increase. According to [37], the best values of contact angle for cell attachment were assessed at  $55^\circ$  and for bone regeneration from  $35^\circ$  to  $80^\circ$ , just like here.

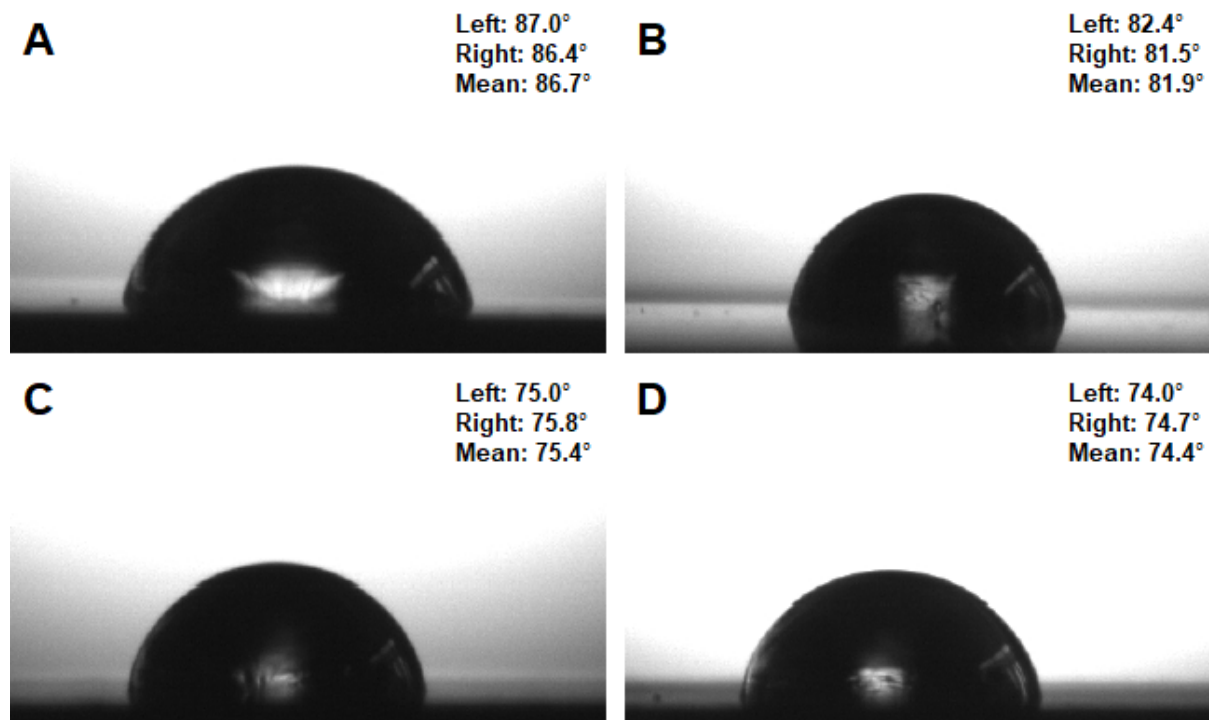


Fig. 7. Wettability of material for: A - MR, B - L1 laser treatment, C - L2 laser treatment, D - L2 + L1 laser treatment

## CONCLUSIONS

Observations of the surface microstructure using light and SEM microscope confirm the significant modification of the Ti13Zr13Nb alloy surface after laser treatment. It is proved that the use of laser power in the range of 700 - 1000 W and feed speed of 1 mm/s results in a laser-modified layer of a small depth or local lack of remelting. With the increase of the laser pulse power, the further change in the surface microstructure and the number of defects is observed. The use of double treatment 1000 W + 700 W allows to reduce the number of defects in the form of cracks.

Laser modification of the Ti13Nb13Zr alloy results in the increase of mechanical properties, such as Young's modulus and nanohardness about the native material substrate. The hardness increases by almost 90% after applying the laser modification 1000 W. The use after this treatment of the second surface pass at a lower 700 W pulse power (motivated by a better microstructure) results in a slight softening of the material. It may be attributed to some processes of melting, diffusion and recrystallization. This treatment significantly influences the unification of mechanical properties within the tested surface, which is essential for the behavior of the material under the influence of various loads.

The increase in the roughness Ra parameter, which has a positive effect on the increase of implant material integration with the bone tissue and on its mineralization, can be observed depending on the laser pulse power. The roughness increases for the applied power of 700 W almost twice, of 1000 W - almost three times and for 1000 W + 700 W - four times.

The reduction of the contact angle following the increase in the laser power parameter increases the hydrophilicity of the material, and thus improves its biological properties.

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