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MICROSTRUCTURE AND MECHANICAL PROPERTIES OF LASER SURFACE-TREATED Ti13Nb13Zr ALLOY WITH MWCNTs COATINGS

ABSTRACT

Laser surface modification of titanium alloys is one of the main methods of improving the properties of titanium alloys used in implantology. This study investigates the microstructural morphology of a laser-modified surface layer on a Ti13Nb13Zr alloy with and without a carbon nanotube coating deposited by electrophoretic deposition. Laser modification was performed for samples with and without carbon nanotube coating for two different laser powers of 800 W and 900 W and for different scan rates: 3 mm/s or 6 mm/s at 25 Hz, and the pulse duration was 2.25 ms or 3.25 ms. A scanning electron microscope SEM was used to evaluate the surface structure of the modified samples. To observe the heat-affected zones of the individual samples, metallographic samples were taken and observed under an optical microscope. Surface wettability tests were performed using a goniometer. A surface roughness test using a profilograph and a nanoindentation test by NanoTest™ Vantage was also performed. Observations of the microstructure allowed to state that for higher laser powers the surfaces of the samples are more homogeneous without defects, while for lower laser powers the path of the laser beam is clearer and more regular. Examination of the microstructure of the cross-sections indicated that the samples on which the carbon nanotube coating was deposited are characterized by a wider heat affected zone, and for the samples modified at 800 W and a feed rate of 3 mm/s the widest heat affected zone is observed. The wettability tests revealed that all the samples exhibit hydrophilic surfaces and the samples with deposited carbon nanotube coating increase it further. Surface roughness testing showed a significant increase in Ra for the laser-modified samples, and the presence of carbon nanotubes further increased this value. Nanoindentation studies showed that the laser modification and the presence of carbon coating improved the mechanical properties of the samples due to their strength.

Keywords: *Ti13Nb13Zr alloy, laser alloying; carbon nanotubes; contact angle; nanoindentation*

INTRODUCTION

During the past years, there has been observed an increasing number of people demonstrating several problems with their bones such as osteoporosis or osteoarthritis. The biomaterial industry is constantly evolving and the target of prostheses is growing due to the fact that an aging society would like to be active as long as it is possible. Researchers work on high quality biomaterials also for dental implants. The main goal of implants producers is to extend durability while at the same time ensure a short time of integration of the implants with the body. Due to prostheses, elder people can stay active longer [1,2].

The most commonly used biomaterials in orthopedics and dentistry are titanium alloys, cobalt-chromium alloys, magnesium-based alloys, and stainless steel [3]. The value of Young's modulus for titanium is about 100 GPa, while this index for human bone ranges from 3 to 40 GPa depending on the type of bone tissue. Titanium alloys have an advantage over pure titanium in that alloying elements reduce the value of Young's modulus, making it similar to that of human bone [1,3,4]. Titanium alloys are light materials and have good strength properties [5]. The tissue engineering is based on Ti6AlV, Ti6Al7Nb, and Ti13Nb13Zr [6]. Aluminium-containing alloys have been characterized by higher toxicity than Ti13Nb13Zr alloy [7]. The content of both aluminium and vanadium can cause neurological problems; vanadium ions were shown to cause cytotoxic reactions, while aluminium ions showed the effect of bone softening [8].

Titanium surfaces can be modified by coatings applied to the substrate by plasma spraying [9], sol-gel method, and electrophoretic deposition [10]. Performing a hybrid modification consisting of coating deposition followed by laser modification makes it possible to improve material properties [11]. The validity of the laser as a heat source is related to its widespread use for welding and surface modification [12]. The use of a laser beam for modification is advantageous due to the reproducibility of the process and the possibility of precise determination of the modification area [13]. In addition, the use of a laser beam guarantees high power density, low heat consumption, and at the same time a small penetration depth [14]. Nowadays the most popular hybrid modification is plasma spraying with laser modification in situ [11]. For all thermal spray technologies their limitation is adhesion between the substrate and the coating. An increase in adhesion for laser modified coatings has been often demonstrated [13,14]. Laser melting of the coating further unifies the structure and increases its microhardness. Moreover modified by laser melting increase osseointegration for implants in human body [15]. In addition, conducting the laser modification at the same time as the coating deposition allows to reduce the time of the whole operation.

Electrophoretic coating deposition has an advantage over plasma spraying. The technique is simple, easily accessible, and quick to make. A uniform coating can be deposited using constant parameters of the solution while keeping the same conditions like temperature and voltage of the process [16]. The spectrum of EPD applications includes industries such as electronics, film-voltaic, automotive, and the very rapidly growing medical industry [17–19]. Electrophoretic deposition is possible for a variety of substrates and shapes, which is important for the medical industry given the currently high personalization of devices [20].

In the field of orthopedics and stomatology, the materials used for coatings are usually carbon materials, hydroxyapatite or chitosan, or composites of these materials. In the group of carbon materials, carbon nanotubes represent a material with good surface properties that allow them to be used as substrates for tissue growth. In addition, the chemical composition of nanotubes is similar to the composition of the extracellular matrix [21,22]. A study [23] proves that the presence of carbon nanotubes improves the viability of osteoblasts and increases their adhesion to the substrate. Moreover, carbon nanotubes show the ability to stimulate and differentiate stem cells towards osteoblasts, which is advantageous for bone regeneration after injury. Present studies focus on laser modified carbon nanotube composites with iron [24], or aluminum [25]. In another report [24] as a result of remelting an iron-carbon nanotube composite with a Nd:YAG laser, a greater dispersion of carbon nanotubes appeared at 800 W of power than at 600 W, which also increased the hardness of the material.

The research presented in this paper continues the search for the best laser processing parameters for Ti13Nb13Zr alloy with carbon coating in the context of using this modification for biomedical applications. In work [1] it was proved that laser modification in combination with carbon coating provides obtaining hydrophilic surface and mechanical properties are dependent on laser processing parameters. Depending on them, the microstructure of the surface layer of the material also changes, and this affects, among others, the corrosion resistance. This paper presents the results of investigations of mechanical properties, contact angle, and microstructure for 800 and 900 W power at different scanning speed and laser pulse duration. The results confirmed the increase of mechanical properties (measured on the surface) and hydrophilic character of the surface already for such selected parameters.

MATERIALS AND METHODS

Ti13Nb13Zr alloy rod, provided by a commercial supplier (Xi'an SAITE Metal Materials Development Co., Ltd., Xi'an, China), has the composition shown in Table 1. Four quarters formed from a 40 mm diameter rod were used in this study. Samples were sanded with the abrasive papers Nos. 220, 500, and 800 in gradation with a metallographic grinding machine (Saphir 330, ATM GmbH, Mammelzen, Germany). After grinding, the samples were washed in distilled water and dried in the air.

Table 1. *Chemical composition of the Ti13Nb13Zr alloy in % by weight*

Element	C	O	N	Fe	Nb	Zr	Ti
Content	0.04	0.11	0.019	0.05	14.001	13	Balance

Three of six samples were washed in acetone, distilled water, and 5% hydrofluoric acid. On these samples, carbon nanotubes (MWCNTs) were embedded by the electrophoretic deposition method.

Before electrophoretic deposition, the carbon nanotubes (MWCNTs, 3D-Nano, Krakow, Poland) were functionalized. In the first step, the powder of MWCNTs was heated up to 400°C for 8 h. Next MWCNTs were heating up in a solution of acid: HF and HNO_3 a ratio of 3:1 for 3 h in 70°C. After that the acid suspension was gradually diluted with water, centrifuged, the acid was decanted and water was added, repeating this procedure until a neutral pH was obtained. Then, the suspension was diluted to get thin coatings of carbon nanotubes, down to the content of MWCNTs 0.15 wt. pct.

The electrophoretic deposition was carried out at stable parameters: voltage 20 V, time of electrophoretic deposition was 30 s, and distance between samples was 10 mm. Electrodes were placed parallel to each other at a distance of about 10 mm. The sample of the Ti13Nb13Zr alloy constituted an anode and the platinum plate was a cathode. The electrodes were connected to the DC power supply (SPN 10-01 C, MCP, China).

For surface modification, the pulse laser Nd: YAG (TruLaser Station 5004, TRUMPF, Germany) was used for each sample (Table 2). Samples T1, T2, and T3 are samples of titanium alloy Ti13Nb13Zr machined and then modified with a laser beam according to the parameters in Table 2. Samples C1, C2 and C3 are samples of titanium alloy with deposited carbon nanotube coating. The laser treatment was performed under protective gas, argon content of not less than 99.987% for the proper course of remelting the substrate, to minimize the risk of oxidation. A laser modification with a laser power of 800 W and 900 W was selected based on the results of the work [6,26] and previous studies by the authors.

Table 2. *Parameters of laser melting and nanoindentation test of the Ti13Nb13Zr alloy*

Laser melting				
Sample	Power of the laser pulse [W]	Scan rate [mm/s]	Duration of the laser pulse [ms]	Frequency [Hz]
T1, C1	800	6	3.25	25
T2, C2	800	3	3.25	25
T3, C3	900	6	2.25	25
Nanoindentation test				
Maximum force [mN]		50		
Loading and unloading times [s]		20		
Dwell period at maximum load [s]		10		
Relife time [s]		20		

An optical microscope (UC50, Olympus Europa SE & Co. KG, Hamburg, Germany) was used to observe modified surfaces. Next, metallographic sections/microsection were examined with the optical microscope and scanning electron microscope SEM (JSM-7800F, JEOL, Tokyo, Japan)

Determination of wettability was carried out for every sample after laser modification. The contact angle measurement was made using a goniometer (Contact angle goniometer, Zeiss, Ulm, Germany). The measurements of the contact angle were carried out in 10 s at room temperature.

The roughness measurement of the modified surface was performed at the distance of 4 mm using a profilograph Hommel Etamic Waveline (JENOPTIK). Each result of the roughness parameter (Ra) is the average arithmetic of three measurements.

Nanoindentation tests were performed with the NanoTest™ Vantage (Micro Materials, Great Britain) using a Berkovich three-sided pyramidal diamond. The main parameters of nanoindentation tests was presented in Table 2. During the indent, the load-displacement curve was determined using the Oliver and Pharr method. Based on the load–penetration depth curves, the surface hardness (H) and Young's modulus (E) were calculated using integrated software. Estimating Young's modulus (E), the Poisson's ratio of 0.25 was assumed for carbon nanotube coating and 0.36 for Ti13Nb13Zr alloy.

RESULTS AND DISCUSSION

Fig. 1 shows images of the surface microstructure of a laser-treated Ti13Nb13Zr alloy with and without a carbon nanotube coating. The images, obtained using electron microscopy (SEM), indicate the presence of a laser path for each sample. There are noticeable differences in the melts made at a feed speed of 3 (T2, C2) and 6 mm/s (T1, C1, T3, C3). The most regular laser path is observed for T1 and T2 samples. The surface microstructure of the carbon nanotube-coated samples shows a more subtle outline of the laser path. Numerous precipitates are visible on samples T3 and C3 and the laser path is irregular; these melts were made at higher laser power than samples T1, C1, T2, C2. In paper [6], it has been shown that the use of double laser modification of the sample results in a reduction in the number of etchings and cracks on the surface. The T3 and C3 samples that were modified with higher laser power have the lowest number of impurities and cracks also as in [26]. In [27] study, the time of the laser pulse was changed; as the duration increased, the surface roughness decreased, concluding that more intense (in terms of laser power or laser pulse duration) contact between the sample and the laser results in reduced cracking.

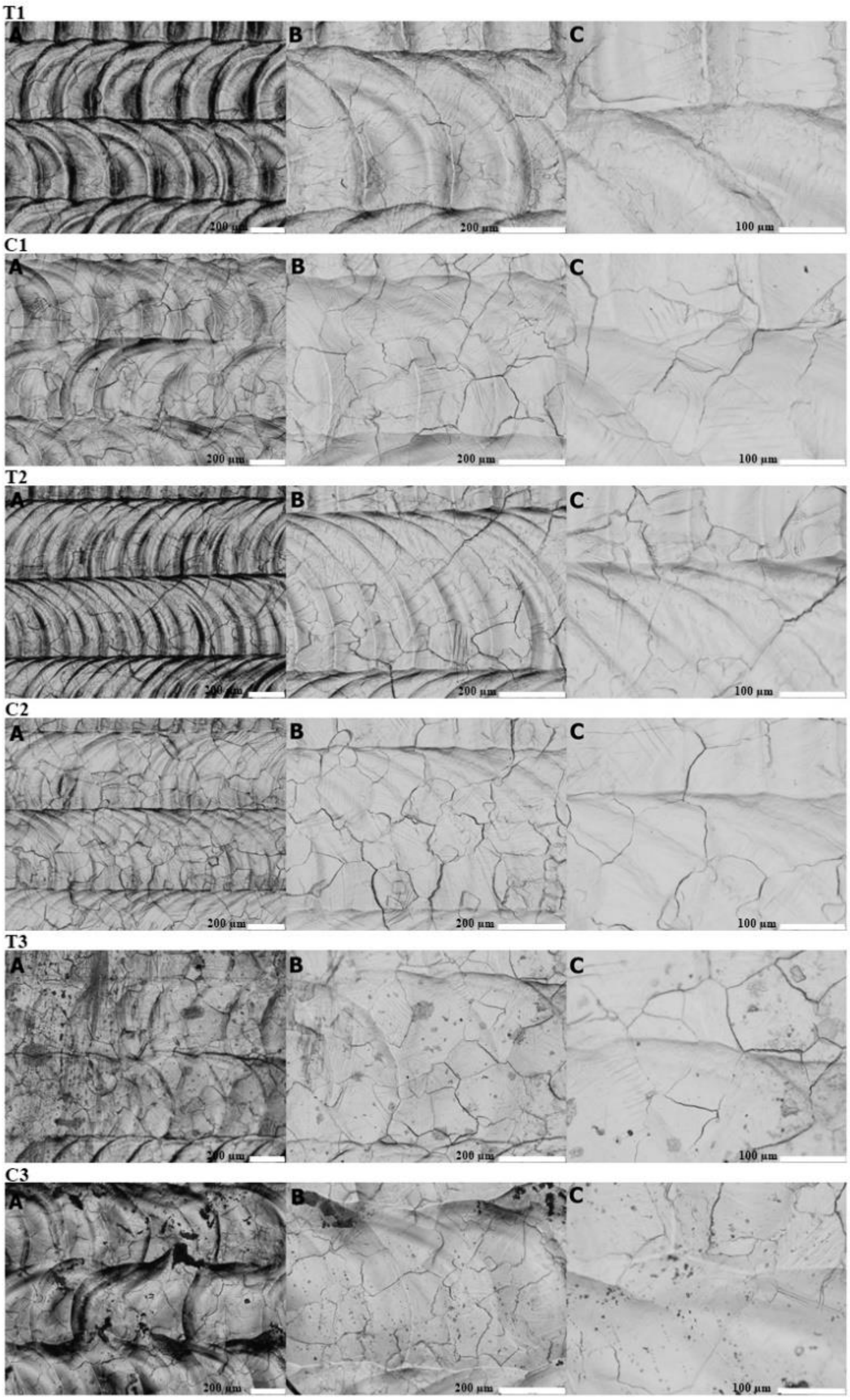

Fig. 1. Surface microstructure of the Ti13Nb13Zr alloy after laser modification, T1, C1 – 800 W, 6 mm/s, 3.25 ms; T2,C2 – 800 W, 3 mm/s, 3.25 ms; T3,C3 – 900 W, 6 mm/s, 2.25 ms

For each sample (Fig. 1), the boundaries of the heat affected zone are visible, which vary with the modification parameters. Observation with an optical microscope allowed us to measure the depth of remelting (Table 3) for individual samples. Samples T1, C1, and T3, C3 are characterized by similar remelting depths, with the samples on which the carbon nanotube coating was previously deposited showing a larger heat-affected zone, which we can see in Fig. 2. For T2 and C2 samples, the depth of remelting is significantly higher than for the other samples, which is most likely due to the different, slower passage of the laser beam (not 6 mm/s but only 3 mm/s).

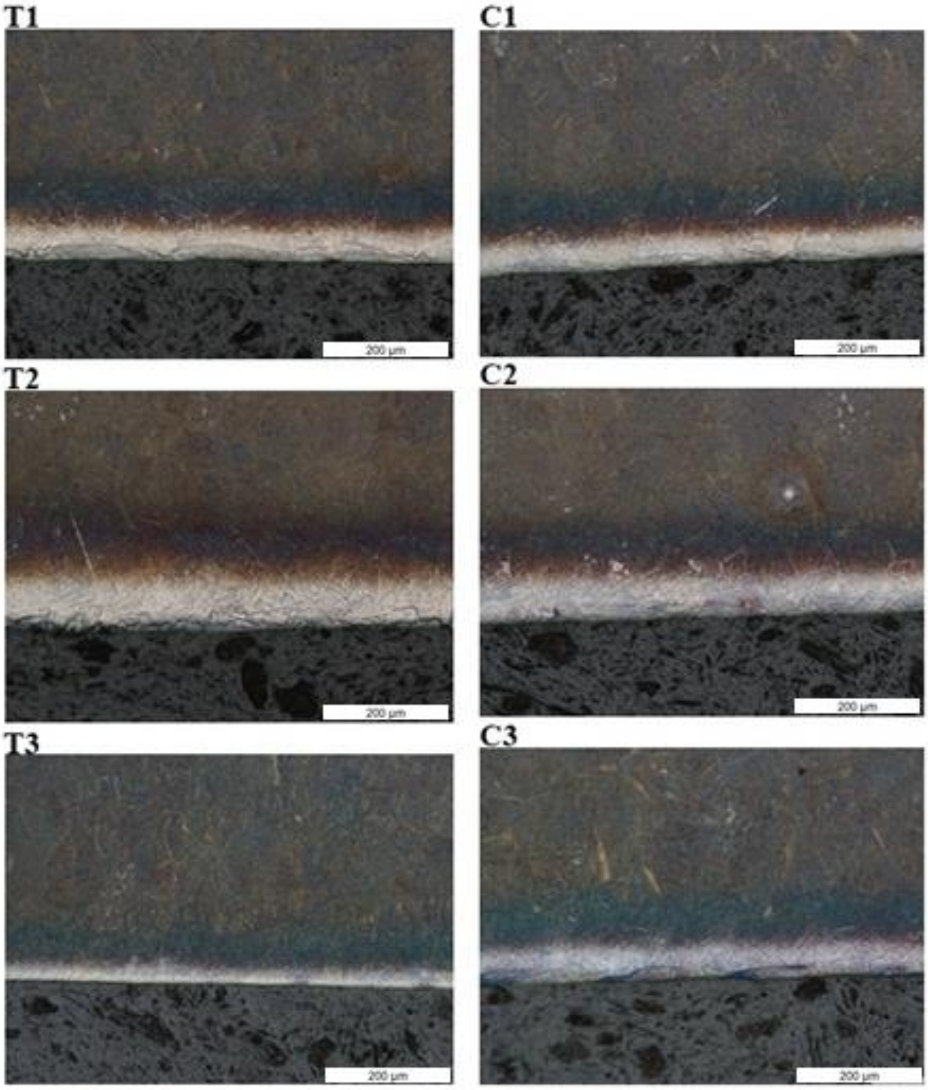

Fig. 2. Cross-section microstructure of laser modified Ti13Nb13Zr alloy, T1,C1 – 800 W, 6 mm/s, 3.25 ms; T2,C2 – 800 W, 3 mm/s, 3.25 ms; T3,C3 – 900 W, 6 mm/s, 2.25 ms

Table 3 shows also the mean contact angle results for each sample. All the samples subjected to the contact angle test exhibit hydrophilic properties. The presence of carbon nanotube coating causes a decrease in the average wetting angle value. The study [3] indicates that the application of coatings on the surface causes a decrease in the contact angle. The accuracy of the statement that the presence of carbon nanotubes decreases the wetting angle value is confirmed by a study [28], where carbon nanotubes were deposited on titanium using an electrophoretic deposition method for 30 s at 30 V. The results indicated that the contact angle was reduced due to the presence of carbon nanotubes from 76° to 30°. In [29] it was also pointed out that the presence of carbon nanotubes increased the wettability of the sample, from 70.07° to 56° The decrease in the contact angle value for carbon nanotube coated samples is very beneficial in the aspect of implantology because nanotubes accelerate the osseointegration process and hydrophilicity also benefits the cell adhesion [28]. In addition, as the laser power increases, a decrease in the value of the averaged wetting angle occurs, which was observed in the study [7], where the contact angle was reduced from 87° to 75° for a single laser treatment and to 74° with double laser modification. The contact angle values obtained for the samples modified in this work are lower, which confirms that the application of laser modification increases the wettability of the material. Moreover, the samples coated with carbon nanotubes showed lower values of contact angle than samples without carbon nanotubes coating (Table 3). In the study [30] it was found that the values of the wetting angle in the range from 30 to 80° were the best for bone regeneration. The results for the contact angle in this work are in the close range were obtained in the present work.

Table 3. *Melting depth and contact angle for laser-modified Ti13Nb13Zr alloy samples*

Laser melting		
Sample	Melting depth μm	Contact angle
unmodified Ti13Nb13Zr [6]	-	87˚
Ti13Nb13Zr with MWCNTs coating [29]	-	56.50˚
T1	192.10	78.06˚
C1	196.86	82.50˚
T2	230.20	81.76˚
C2	242.42	80.39˚
T3	106.76	79.13˚
C3	196.18	74.26˚

Table 4 shows the surface roughness (Ra) results for the laser treated samples with and without nanotube coating and Fig. 3 shows their roughness profiles. The roughness profile for each of the laser modified samples relative to the base material is larger (Table 4). Additionally, for the samples modified by laser at 800 W, the Ra parameter is higher for the samples without deposited carbon nanotube coating. While as the laser power increases up to 900 W, the surface roughness increases relative to the samples modified at 800 W, but also the increase in laser power resulted in higher roughness for sample C3 with carbon nanotube coating than without the coating (T3). The paper [6] also shows an increase in roughness with increasing laser power during modification.

Table 4. *Laser treatment and roughness parameters of examined samples*

Sample	Power of the laser pulse W	Duration of the laser pulse ms	Scan rate mm/s	Ra μm
unmodified Ti13Nb13Zr [6]	-	-	-	0.65
T1	800	3.25	6	2.00
C1	800	3.25	6	1.67
T2	800	3.25	3	1.67
C2	800	3.25	3	1.35
T3	900	2.25	6	0.63
C3	900	2.25	6	2.80

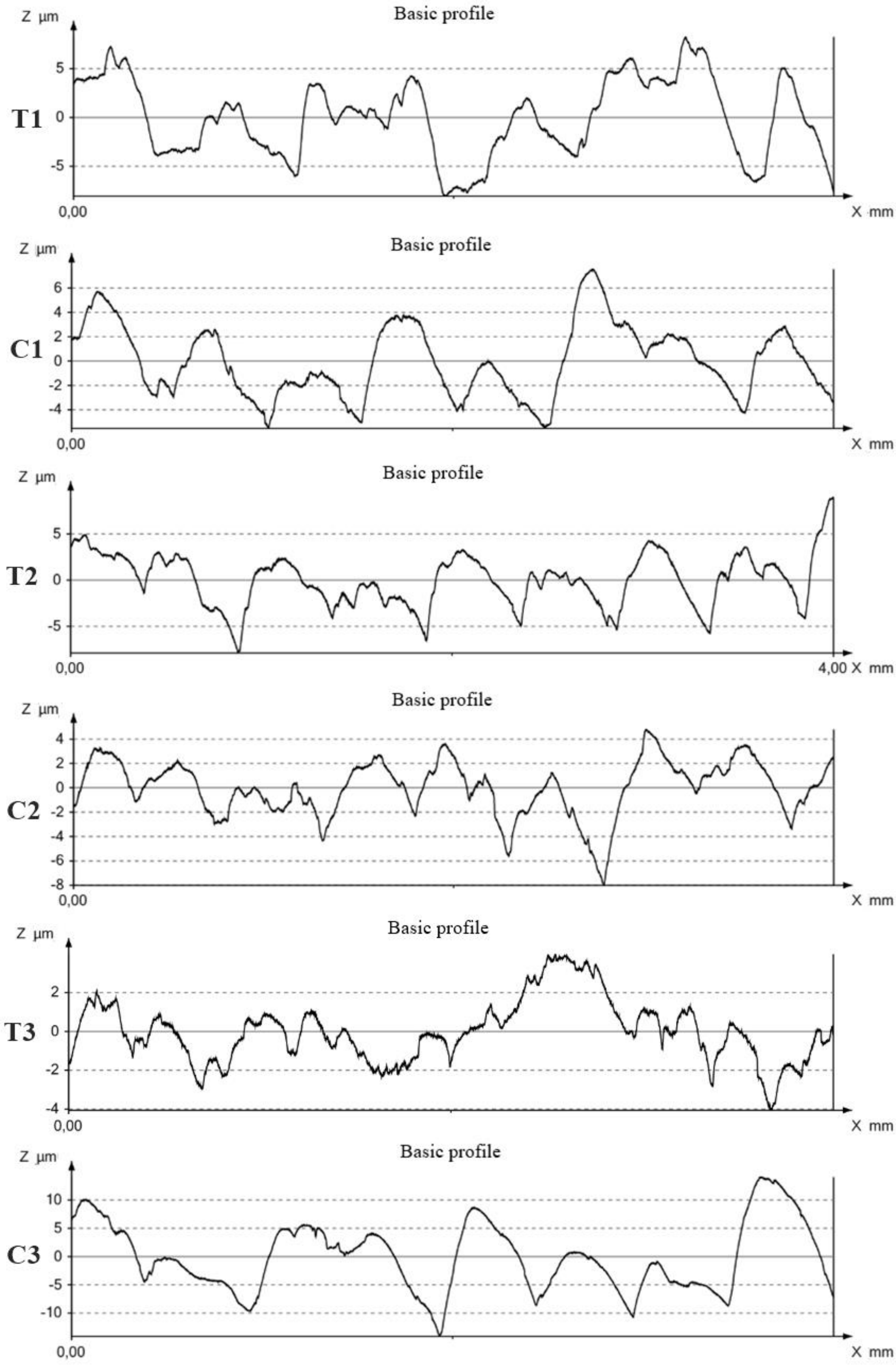

Fig. 3. Roughness profiles for T1,C1 – 800 W, 6 mm/s, 3.25 ms; T2,C2 – 800 W, 3 mm/s, 3.25 ms; T3,C3 – 900 W, 6 mm/s, 2.25 ms

After performing the nanointendation test, a 3D distribution was created for Young's modulus and nanohardness. The data relating to nanoindentation, Young's modulus, reduced Young's modulus and maximum indent depth were collected in Table 5. Figs. 4 and 5 representing the distributions on Young's modulus and nanohardness indicate that as the laser power increases for samples without carbon nanotube coating, there is a uniform distribution of the values of these parameters. In the case of samples with carbon nanotube coating, this distribution, with the increase of laser power, in comparison to the parent material with coating, is irregular for both Figs. 4 and 5. For each of the samples with and without carbon nanotube coating, an increase in the values of Young's modulus and nanohardness in comparison to the parent material is observed (Table 5). The increase of these values is even two times. The samples modified at the same laser power but at different feed rates show that the feed rate of 3 mm/s influences the increase of nanohardness and Young's modulus. For laser power of 800 W, the samples with the coating (C1, C2) show lower values of investigated parameters, while the increase of laser power to 900 W caused that the sample C3 with carbon nanotube coating showed the highest nanohardness, the highest value for Young's modulus at 900 W laser power and in relation to the other samples with coating C1 and C2, at the lowest maximum indent depth. In research [6] it has been proved, as for the above results, that increasing the laser power decreases the maximum indent depth and also increases the value of Young's modulus and nanohardness. Analogous relations were also shown in work [1].

Table 5. *Mechanical properties and maximum indent depth for the substrate, laser modified Ti13Nb13Zr alloy with and without carbon nanotubes coatings*

Sample	Nanohardness (H) GPa	Reduced Young's Modulus (E_r) GPa	Young's Modulus GPa	Maximum indent depth nm
Unmodified Ti13Nb13Zr [6]	20.62 ±14.2	279.09 ± 134.39	341.84 ± 237.11	441.38 ± 197.49
T1	47.61 ±9.23	415.78 ± 65.58	580.81 ± 152.21	243.65 ±22.97
C1	64.37 ±21.1	371.1 ± 71.37	488.89 ± 119.23	249.54 ±80.29
T2	48.25 ±17.77	389.18 ± 118.29	554.58 ± 285.2	259.42 ±62.61
C2	55.7 ±25.04	347.58 ± 93.42	451.69 ± 157.38	268.21 ±79.35
T3	33.92 ±18.42	329.92 ± 122.16	435.13 ± 226.01	340.06 ± 159.62
C3	68.52 ±18.53	390.19 ± 59.32	523.15 ± 111.95	233.92 ±48.78

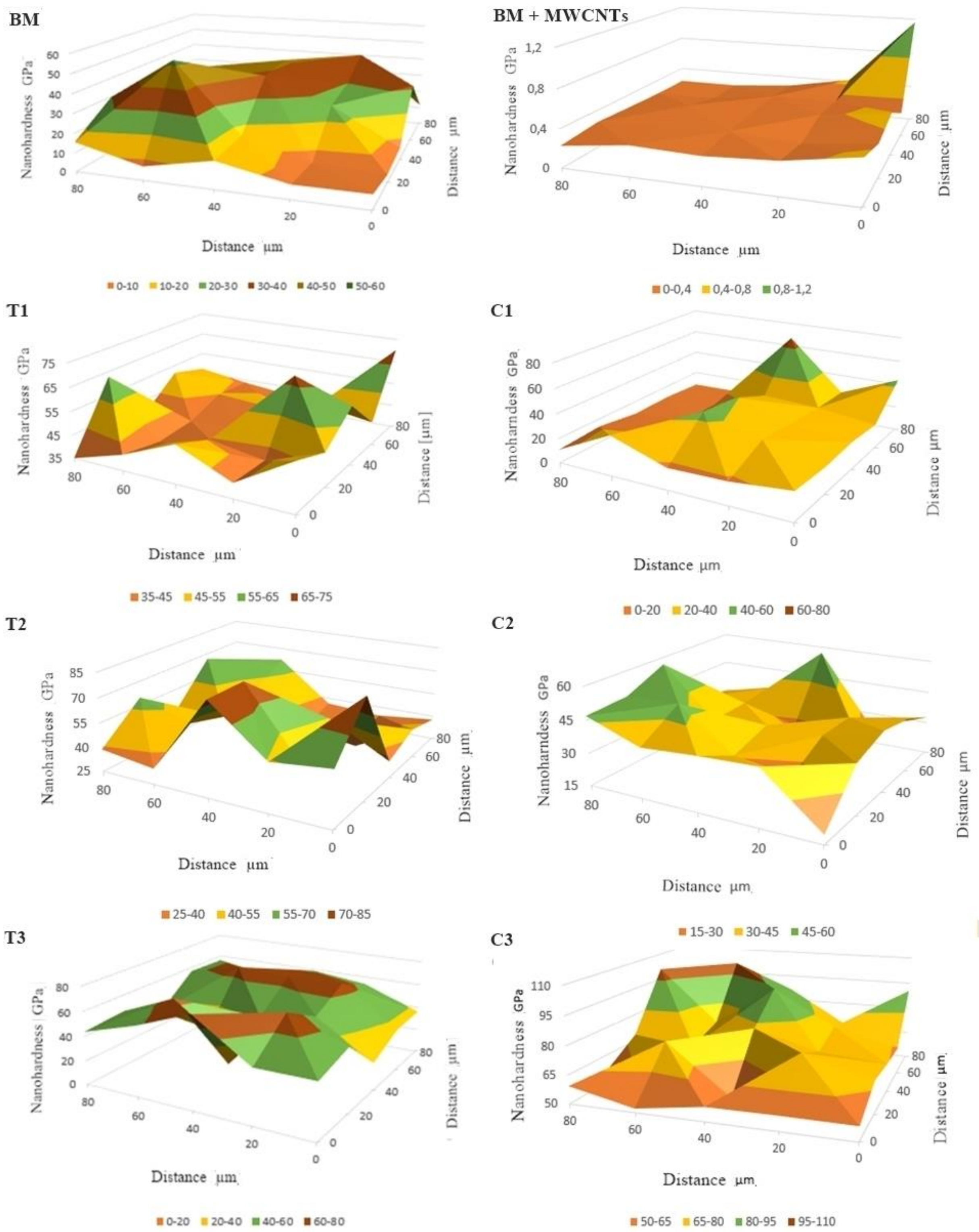

Fig. 4. 3D distribution of nanohardness for BM – base material, BM +MWCNTs – base material with carbon nanotubes coating, T1, C1 – 800 W, 6 mm/s, 3.25 ms; T2, C2 – 800 W, 3 mm/s, 3.25 ms; T3, C3 – 900 W, 6 mm/s, 2.25 ms

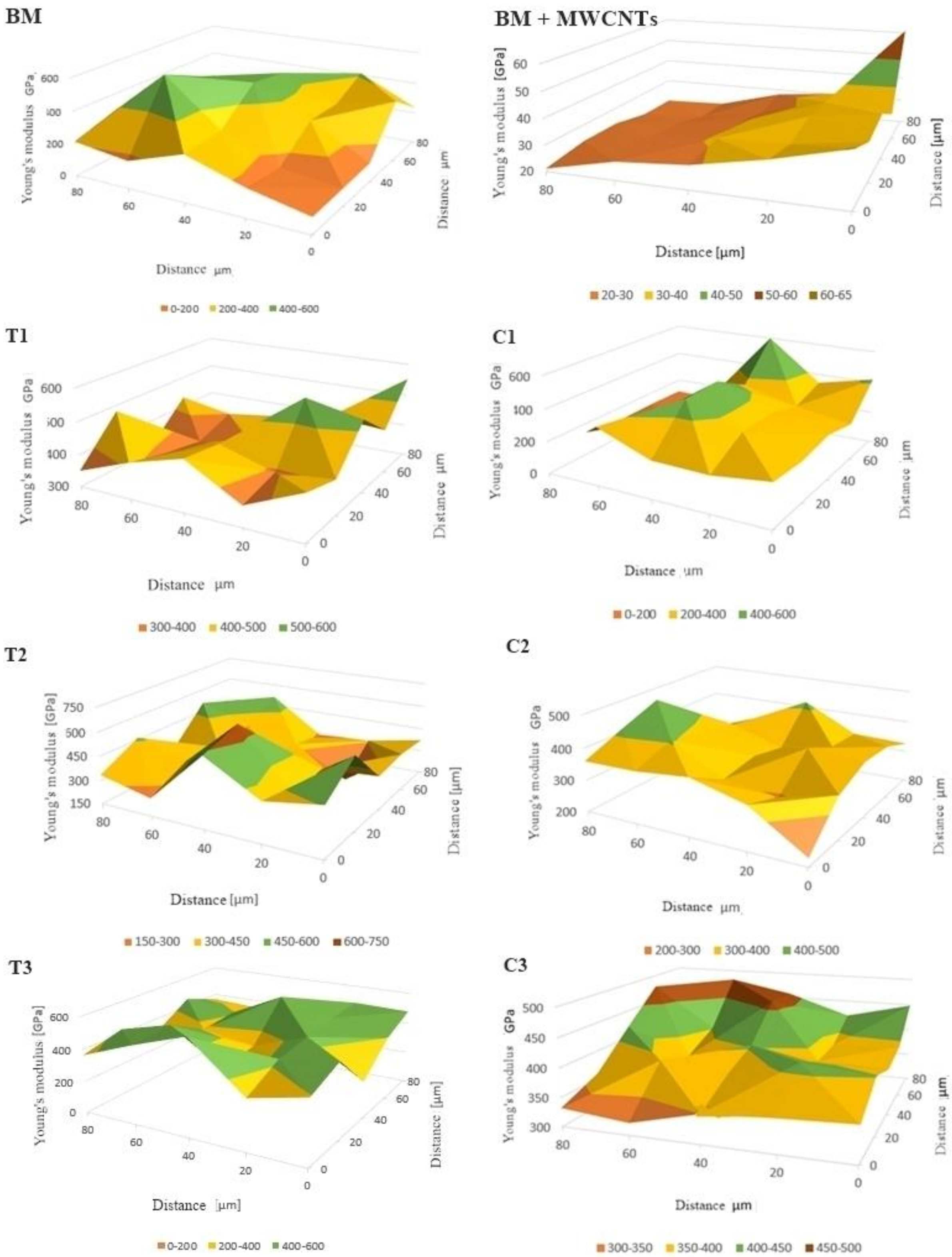

Fig. 5. 3D distribution of Young's modulus for BM – base material, BM + MWCNTs – base material with carbon nanotubes coating, T1,C1 – 800 W, 6 mm/s, 3.25 ms; T2, C2 – 800 W, 3 mm/s, 3.25 ms; T3, C3 – 900 W, 6 mm/s, 2.25 ms

SUMMARY

Microstructure observations of Ti13Nb13Zr samples with and without MWCNTs coating show the effect of laser modification on surface wettability. It is indicated that the depth of heat influence for the samples with a coating of carbon nanotubes is higher than for uncoated samples. The samples modified with 900 W laser power have fewer precipitates and cracks. As the laser modification power increases, a decrease in the mean wetting angle value is observed. The laser treatment increases the wettability because of the reduction of roughness. In addition, the presence of carbon nanotube coating further decreases the wetting angle value. The results of surface roughness and wettability suggest that cell adhesion to the modified surface will increase, thus accelerating osteointegration. An improvement of the mechanical properties: nanohardness and an increase in Young's modulus were observed for each sample subjected to laser modification. The increase in laser power and the presence of carbon nanotube coating caused the largest increase in the parameters studied. The surface roughness of the samples also increased with increasing laser power.

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