Technological parameters optimization in picosecond laser texturing of titanium surfaces

T D Dikova¹ ²*, S A Kulinich², S Iwamori¹ ² and S Yamaguchi²

¹ Medical University of Varna, 55 Marin Drinov Str., 9000 Varna, Bulgaria
² Tokai University, 4-1-1 Kitakaname, Hiratsuka-shi, Kanagawa, 259-1292 Japan

*E-mail: tsanka.dikova@mu-varna.bg

Abstract. The present paper deals with studying the surface morphology of commercially pure (cp) Ti Gr-2 and Ti6Al4V treated by a picosecond laser and with determining the optimal technological parameters for fabricating cavities with a regular shape and a depth of about 10 μm. The surfaces of disk-shaped samples were treated by a commercial picosecond laser with a power of 0.2 W, 0.5 W and 1 W and a number of pulses between 1,000 and 20,000. The samples’ surface was investigated by SEM and a non-contact 3D surface profiler. The technological parameters were optimized by regression analysis using the QStatLab software. It was found that after laser treatment with the lowest values of the above parameters only the surface roughness changed in the case of cp-Ti, while its Ti6Al4V counterpart had a “melted zone” with a 5.5-μm depth. Raising the values of the regime parameters mainly led to an increased cavity depth on the cp-Ti surface, while those on Ti6Al4V increased in all dimensions. The surface roughness of both materials was higher after the laser treatment and grew bigger as the laser power and the number of pulses were increased. The optimal technological parameters for treatment of cp-Ti and Ti6Al4V were found. The results obtained can be used for picosecond laser texturing of titanium surfaces using linear or dimple types of patterns.

1. Introduction
Titanium and its alloys are the most preferable materials for implants production [1-5]. Pure titanium is characterized by high corrosion resistance and biocompatibility. It also possesses mechanical properties and elastic modulus close to that of the bone tissues, thus contributing to its very good osteointegration. The Ti6Al4V alloy is mostly used for dental and orthopedic implants due to its higher tensile and yield strength compared with pure titanium [6-10]. Apart from the bulk properties, the surface properties of material, such as surface chemistry, topography and roughness, also play an important role in good implant osteointegration [7, 9-11]. This is why the surfaces of implants are treated and modified by different methods (chemical, mechanical or electro-chemical) [5, 8, 9, 12]. Lately, laser surface treatment has been used for this purpose because it is a fast, contactless, environmentally friendly, and easy to operate and control approach. Additionally, it offers the possibility of modifying surfaces of complex shape at a micro/nano-level [13-15]. Of all lasers available, those with femtosecond or picosecond pulse duration are usually preferred over the nanosecond-pulse lasers as they can provide a higher precision and a negligible heat-affected zone around the treated area [5, 9, 11].

Using lasers, titanium surfaces can be modified by different patterns: with dimples or linearly with varying dimensions [7, 8, 10, 11, 16, 17]. This always leads to increased surface area and wettability,
which could improve the cell attachment, cell differentiation and growth [11]. On the other hand, the linear pattern ensures “contact guidance” for the cells to align along the micron-sized linear grooves formed on the surface, which can enhance the osteointegration and increase the implant longevity [9, 10, 12]. Additionally, the grooves can “interlock” the implant with the new bone, thus improving its stability.

At present, one still finds contradictory data about the surface texture dimensions that enhance the titanium implants’ biocompatibility. After implant placement, the processes run at multiple levels [10, 12]: (i) at a nanoscale, where cell microtubules interact and form focal adhesion complexes; (ii) at micron and sub-micron levels with cells alignment and (iii) at a macroscale, where organs and tissues interact along larger surface contours. It is known that the cell contact guidance on laser treated Ti6Al4V surfaces is caused by nano- and micro-scale roughness that provide sites for focal point adhesion, thus ensuring the following cell alignment [16]. According to Mirhosseini N. et al. [7], the optimum surface roughness that provides the highest cell growth is related to the actual cell size, i.e. it is in the micron size range. Mukherjee S. et al. modified Ti6Al4V and reported that its surface features with sizes closer to cell dimensions could positively affect the viability and spreading of MG63 cells [12]. Erdoğan and co-workers found that a texture consisting of holes with a diameter of 40 μm in and depth of 15 μm reduced significantly the cells attachment and proliferation [9]. Meanwhile, for dental implants it was claimed that the depth of micro-grooves should be in the range of 100 μm, since this value corresponds to the mean size of human gingival fibroblasts [8]. Hirao M. et al. established that grooves of 500 μm in width had a significant effect on the bone-metal shear strength [18]. Hall and colleagues also indicated that grooved implants (with grooves 110 μm and 200 μm wide and 70 μm deep) could stimulate bones to form preferentially along the grooves. However, most authors conclude that the optimal groove depth and width that promote cells integration and contact guidance are in the range of 8 – 12 μm [10, 11, 16, 17].

Therefore, the aim of the present work is to investigate the surface morphology of commercially pure (cp) Ti Gr-2 and Ti6Al4V treated by a picosecond laser, and to determine the optimal technological parameters for producing cavities with a regular shape and a depth of about 10 μm, thus enhancing their biocompatibility.

2. Materials and methods

2.1. Materials and samples preparation

Cp-Ti Gr-2 and Ti6Al4V alloys were used for manufacturing disk samples (24 mm in diameter and 3-mm thick). Their surfaces were ground, polished, ultrasonically cleaned for 15 min consecutively in acetone, ethanol and distilled water, after which they were dried with compressed air. The sample surfaces were then treated by a commercial picosecond Japanese Microchip Laser (Hamamatsu Photonics K.K) in ambient air. The laser (λ = 1064 nm, pulse repetition rate 100 Hz, pulse width 500 ps) was operated in a stationary mode with the laser beam focused on the surface (10-μm spot diameter). During the experiment, two regime parameters were varied: (i) the average power (0.2 W, 0.5 W, 1 W), which determined the pulse energy (2 mJ, 5 mJ, 10 mJ) and the laser energy density (fluence) (2.54 kJ/cm², 6.35 kJ/cm², 12.7 kJ/cm²); and (ii) the number of pulses (1000, 2000, 5000, 10 000, 20 000) [5].

2.2. Samples characterization

The samples’ surface morphology was observed by field-emission scanning electron microscope FESEM (JSM-7100F, JEOL). The arithmetic mean roughness deviation (Rₐ), the maximum height of the profile (Rₛ) and the root-mean-square roughness deviation (Rₐ) of the surface were investigated by a BW-S500/BW-DS500 (Nikon) super high vertical resolution non-contact 3D surface profiler. The average of five measurements in horizontal and five measurements in vertical directions was taken into consideration (figure 1).
2.3. Regression analysis

Our previous research [5] showed that a zone of laser influence (ZLI) is formed on the surface of the two materials subjected to laser treatment (figure 1). It is characterized by changes in the surface morphology. Increasing the laser power and number of pulses was found to lead to the formation of cavities on the surface [5]. For convenience, in the present study the cavities of a certain depth are referred to as a “melted zone” (MZ). To fabricate surface texture with linear or dimple pattern, it is essential to achieve surfaces with symmetrically-shaped MZ, i.e. with equal or similar sizes in two directions \( l = w \). Therefore, using regression analysis we optimized the technological parameters for producing MZs with a minimal length \( l \), a maximal width \( w \) and a depth \( d \) of about 10 µm.

![Figure 1. SEM image – a), 2D view – b) and cross sections of the surface profile of cp-Ti treated by picosecond laser (0.5 W and 5000 pulses).](image)

**Table 1.** Governing factors and their levels.

| Governing factors | Levels of the factors |
|-------------------|-----------------------|
|                  | Coded                 |
|                  | \( x_1 \) \(-1\) \(-0.25\) \(-1\) |
|                  | \( x_2 \) \(-1\) \(-0.579\) \(-1\) |
| Naturals \( x_j \) | Coded \( x_j \)  | Natural |
| Power \( P_{[W]} \), \( x_j \) \( x_j \) | \( x_j \) \( 0.2 \) \( 0.5 \) \( 1 \) |
| Impulses \( I, x_j \) | \( x_j \) \( 1000 \) \( 5000 \) \( 20000 \) |

**Table 2.** Experimental design.

| No | \( P, x_j \) | \( I, x_j \) | Pure titanium | Ti6Al4V alloy |
|----|-------------|-------------|---------------|--------------|
|    | \( F_1 \) | \( F_2 \) | \( F_3 \) | \( F_1 \) | \( F_2 \) | \( F_3 \) |
| 1  | \(-1\)  | \(-1\)  | 0  | 0  | 0  | 5.5 | 172 | 58  |
| 2  | \(-0.25\)  | \(-1\)  | 2.6 | 204 | 39 | 8.9 | 195 | 121 |
| 3  | 1  | \(-1\)  | 4.1 | 215 | 43 | 16.8 | 287 | 182 |
| 4  | \(-1\)  | \(-0.579\)  | 2.7 | 228 | 43 | 5.8 | 192 | 63  |
| 5  | \(-0.25\)  | \(-0.579\)  | 12.7 | 255 | 37 | 26.6 | 213 | 139 |
| 6  | 1  | \(-0.579\)  | 15.6 | 220 | 39 | 7.1 | 271 | 165 |
| 7  | \(-1\)  | 1  | 5.4 | 240 | 43 | 5.7 | 220 | 86  |
| 8  | \(-0.25\)  | 1  | 13.9 | 260 | 36 | 9.0 | 229 | 151 |
| 9  | 1  | 1  | 11.0 | 225 | 41 | 9.8 | 275 | 145 |
The governing factors and their levels are listed in table 1. The factors, measured in natural physical units, are marked with $x_i$ and have different dimensions. In order to eliminate the experimental plan’s dependence on the dimensions, the factors $x_i$ were transformed into a coded form $x_i$ through the dependence

$$x_i = \frac{(x_i - \bar{x}_i)}{\bar{x}_{i,max} - \bar{x}_{i,0}}$$

(1)

The objective functions are: $F_1, \mu m$ – depth; $F_2, \mu m$ – length; $F_3, \mu m$ – width. A planned experiment was carried out. The experimental design is shown in table 2.

Regression analyses of the obtained experimental results were carried out using the QStatLab software. For the objective functions $F_i, i = 1, 2, 3$, second order polynomials were chosen since the governing factors were changed at three levels:

$$F_i([X]) = a_0 + \sum_{i=1}^{m} a_i x_i + \sum_{i=1}^{m-1} \sum_{i=1}^{m} a_{ij} x_i x_j + \sum_{i=1}^{m} a_{i} x_i^2,$$

(2)

where $[X] = [x_1, x_2]^T \in \Gamma_s$ is the vector of the governing factors, $\Gamma_s$ is the admissible space of the governing factors and $m$ is their number.

After obtaining equations (2), the following optimization task was set and solved:

$$F_{1, min} \leq F_1([X]) \leq F_{1, max}$$

$$F_2([X^+]) = F_{3, min} < F_3([X])$$

(3)

$$F_2([X^+]) \rightarrow min$$

where $F_{1, min}$ and $F_{1, max}$ are the adopted functional limitations and $[X^+] = [x_1^+, x_2^+] \in \Gamma_s$ is the vector of the optimal governing factors.

3. Results and discussion

3.1. Surface morphology

The surface analysis of the two materials showed that their morphology had changed after treatment by the picosecond laser (figure 2). Treatment with the lowest-energy regime was found to only increase the surface roughness of cp-Ti (figure 3), while for Ti6Al4V there was a cavity with 5.5 $\mu m$ in depth, 58 $\mu m$ in width and 172 $\mu m$ in length (figure 4 and table 1). The first cavity (2.6 $\mu m$ deep, 39 $\mu m$ wide and 204 $\mu m$ long) was only observed on the cp-Ti sample after laser treatment with 1000 pulses at a power of 0.5 W. Increasing the regime parameters was found to mainly result in deeper craters in the case of cp-Ti, while for Ti6Al4V all three dimensions grew bigger. As one can see in figures 3, 4 below, the MZ dimensions of the Ti6Al4V alloy are higher when compared with those on the cp-Ti.
The surface roughness investigation confirmed that the laser-treated samples were characterized by higher values of the parameters $R_a$, $R_z$ and $R_q$ compared with the as-polished counterparts (figure 5). Increasing the laser power and the number of pulses during surface modifications resulted in an increase of the roughness parameters for both treated materials, while this effect was more strongly expressed on the cp-Ti sample.

Figure 2. Zone of influence on the surface of cp-Ti (0.5W) – a), b) and c) and Ti6Al4V (0.2W) – d), e) and f), treated by picosecond laser.

Figure 3. Surface morphology of cp-Ti after laser treatment with different regimes.
Figure 4. Surface morphology of Ti6Al4V after laser treatment with different regimes.

It is well known that the surface morphology of laser-treated material depends on its initial microstructure and thermal-physical properties, as well as on the technological parameters applied [5,9,11,13-15,20]. In our experiments, both materials were treated in the same regimes of picosecond laser irradiation. Therefore, the differences in the cavities dimensions are believed to be due the nearly 2.5 times lower thermal conductivity of Ti6Al4V alloy compared to that of cp Ti [2]. On the other hand, the observed different technological parameters influence on the cavity dimensions can be explained in terms of heat conduction losses and plasma shielding effect, the latter known to take place during treatment by picosecond lasers and to reduce the ablation efficiency [20].
3.2. Regression analysis

Changes of the surface morphology at micron and sub-micron scales were previously reported to result from picosecond laser treatment of cp-Ti and Ti6Al4V [5]. The cavity dimensions were shown to vary with the technological parameters applied. In the present study, we aimed to obtain MZ with a regular shape through optimizing the technological parameters using regression analysis. The results obtained are shown in Table 2. The regression models (2) have the following explicit forms: Eqs. (4-6) for cp-Ti and Eqs. (7-9) for Ti6Al4V alloy.

\[ F_1 = 19.261 + 3.767x_1 + 3.933x_2 - 4.489x_1^2 - 9.694x_2^2 \]  
(4)

\[ F_2 = 346.564 + 24.398x_1 + 47.718x_2 - 39.388x_1x_2 - 63.644x_1^2 - 110.109x_2^2 \]  
(5)

\[ F_3 = 51.572 + 4.795x_1 + 5.741x_2 - 7.105x_1x_2 - 4.311x_1^2 - 14.542x_2^2 \]  
(6)

\[ F_4 = 19.562 + 2.614x_1 - 1.190x_2 - 0.878x_1x_2 - 7.551x_1^2 - 4.869x_2^2 \]  
(7)

\[ F_5 = 223.770 + 38.956x_1 + 10.148x_2 - 13.181x_1x_2 + 14.356x_1^2 \]  
(8)

\[ F_6 = 152.062 + 44.338x_1 + 2.135x_2 - 16.382x_1x_2 - 34.533x_1^2 - 0.792x_2^2 \]  
(9)

In order to estimate the significance of the governing factors and the interaction between them, the factors are presented in a coded form in the corresponding regression model. Each factor is varied in the interval (-1 – +1). Then the coefficients in the model have the dimension of the function, and the absolute values of these coefficients are a measure for the importance of the factors and the interaction between them. Obviously, for cp-Ti, the number of pulses (Table 1) is the more significant of the two factors, as the coefficients in the models corresponding to this factor in coded form are larger. Conversely, for Ti6Al4V alloy, the power is the more significant factor.
Figure 6 shows graphical representations of the dependences (4) – (9). Taking into account the graphics, it can be concluded that the task described by Eq. (3) has a simple solution. The solution is depicted in figure 7. Table 3 shows the optimal governing factors and the corresponding values of the objective functions.

![Figure 6](image1.png)

**Figure 6.** Graphical representation of the objective functions: a) for pure Ti; b) for Ti6Al4V alloy.

![Figure 7](image2.png)

**Figure 7.** Optimal solution: a) for pure Ti; b) for Ti6Al4V alloy.

| Table 3. Optimal governing factors. |
|-----------------------------------|
| $x^*_j$ | $x^*_j \cdot W$ | $x^*_j$ | $x^*_j$ | $F^*_j$, $\mu m$ | $F^*_j$, $\mu m$ | $F^*_j$, $\mu m$ |
| Cp Ti  | -0.451816     | 0.42   | -0.67903 | 4050   | 9.51   | 226.7 | 35.742 |
| Ti6Al4V| -0.9783      | 0.21   | -0.27479 | 7890   | 9.52   | 187.3 | 70.583 |

As a result of the regression analysis, the optimal technological parameters for surface treatment by the picosecond laser used in this study were found to be: power of 0.42 W and 4050 pulses for the cp-Ti and power of 0.21 W and 7890 pulses for Ti6Al4V alloy (table 3). It is expected that applying them will result in cavities with a depth of 9.51 $\mu m$ for cp-Ti and 9.52 $\mu m$ for its alloy, as well as dimensions of 226.7 $\mu m \times 35.742$ $\mu m$ (length $\times$ width) and 187.3 $\mu m \times 70.583$ $\mu m$ for cp-Ti and Ti6Al4V, respectively.

4. Conclusions
The surface morphology was investigated of commercially pure Ti Gr-2 and Ti6Al4V alloy, both treated by a picosecond laser. It was found that laser treatment with the lowest parameters only led to a slight
change in the surface roughness of cp-Ti, while Ti6Al4V sample exhibited “melted zones” as deep as 5.5 μm. Increasing the regime parameters mainly led to deeper cavities in case of cp-Ti, while those on the surface of Ti6Al4V grew bigger in all dimensions. The “melted zone” dimensions of the Ti6Al4V alloy were observed to be larger when compared with those on cp-Ti. The surface roughness of both laser-treated samples was higher compared with their polished counterparts. Increasing laser power and the number of pulses resulted in increased surface roughness of both materials; this was more strongly expressed on the surface of cp-Ti. The optimal technological parameters for treatment of cp-Ti and Ti6Al4V were found. The results obtained can be used for texturing titanium surfaces using linear or dimple patterns by picosecond lasers of a similar type.

Acknowledgements
This research was funded under an agreement between Tokai University (Japan) and the Ministry of Education and Science of Bulgaria.

References
[1] Balazic M, Kopac J, Jackson M J and Ahmed W 2007 Int. J. Nano Biomater. 1 3-4
[2] Lütjering G and Williams JC 2007 Titanium 2 ed. (Springer-Verlag Berlin Heidelberg) p 442
[3] Oshida Y, Tuna E B, Aktören O and Gençay K 2010 Int. J. Mol. Sci. 11 1580-678
[4] Dikova T 2012 Scripta Scientifica Medica 44 23-25
[5] Dikova T, Kulinich SA, Iwamori S, Tei K and Yamaguchi S 2019 Journal of the Technical University of Gabrovo 59 5-11
[6] Tritic M S, Radak B B, Gakovic B M, Milovanovic D S, Batani D and Desai T. 2009 Laser Part. Beams 27 85-90
[7] Mirhosseini N, Crouse PL, Schmidt MJ, Li L and Garrod D 2007 Appl. Surf. Sci. 253 (19) 7738
[8] Hsiao WT, Chang HC, Nanci A and Durand R 2016 Materials & Design 90 891-895
[9] Erdoğan M, Öktем B, Kalayçıoğlu H, Yavaş S, Mukhopadhyay PK, Eken K, Özgören K, Aykaç Y, Tazebay UH and Ilday FÔ 2011 Optics Express 19 10986-10996
[10] Ulerich J P, Ionescu L C, Chen J, Soboyejo W O and Arnold C B 2007 Photon Processing in Microelectronics and Photonics vol. 6458 (International Society for Optics and Photonics) p 645819
[11] Pfleging W, Kumari R, Besser H, Scharnweber T and Majumdar JD 2015 Appl. Surf. Sci. 355 104-111
[12] Mukherjee S, Dhara S and Saha P 2015 Int. J. Adv. Manuf. Tech. 76 5-15
[13] Antoszewski B 2016 Czasopismo Techniczne (Mechanika Zeszyt 3-M 10 3-8
[14] Pou P, Riveiro A, del Val J, Comesaña R, Penide J, Arias-González F, Soto R, Lusquínos F and Pou J 2017 Procedia Manufacturing 13 694-701
[15] Yu Z, Yang G, Zhang W and Hu J 2018 J. Mater. Process. Tech. 255 129-136
[16] Chen J, Ulerich J P, Abelev E, Fasasi A, Arnold C B and Soboyejo W O 2009 Mater. Sci. Eng. C 29 1442-52
[17] Fasasi A Y, Mwenifumbo S, Rahbar N, Chen J, Li M, Beye A C, Arnold C B and Soboyejo WO 2009 Mater. Sci. Eng. C 29 5-13
[18] Hirao M, Sugamoto K, Tamai N, Oka K, Yoshikawa H, Mori Y and Sasaki T 2005 J. Biomed. Mater. Res. A 73 213–222
[19] Hall J, Miranda-Burgos P and Sennerby L 2005 Clin. Implant. Dent. Relat. Res. 7 S76–S82
[20] Semerok A, Salle B, Wagner J F and Petite G 2002 Laser. Part. Beams. 20 67-72