Laser surface modification of titanium - a way to improve its biological properties

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J. Kisała[1], A. Barylyak[2], P. Krzemiński[1], R. Wojnarowska-Nowak[1], B. Cieniek[1], Y. Bobitski[1]

[1]*Faculty of Exact and Technical Sciences, University of Rzeszow, Pigonia 1 Str., 35-310 Rzeszow, Poland*
[2]*Danylo Halytsky Lviv National Medical University, Pekarska Str. 69, Lviv, 79010, Ukraine*

INTRODUCTION

Titanium and its alloys are most widely used for load-bearing metal implants due to their good tolerance by living tissues as well as their capability of osseointegration promotion [1, 2]. Key challenges are sub-optimal bone integration in compromised bone conditions and impaired trans-mucosal tissue integration in the presence of a persistent oral microbial biofilm [3]. The ability of the lasers to precisely change the surface features of a material and hence its interaction with the surroundings allows to improve the material's behaviour with biological systems. Depending on the laser parameters, various structures can be created, such as laser-induced periodic surface structures (LIPSS), grooves and spikes (Fig. 1).

Depending on the laser parameters, the obtained structures differ in roughness, wettability, chemical composition, photocatalytic activity, biocompatibility, and antibacterial properties [4]. Modification of the surface with a laser pulses of various energy values promotes the formation of different pattern on the surface and chemical composition of surface. The LIPSS structures showed excellent properties in inhibiting bacterial adhesion, whereas groves were nontoxic and supported cell adhesion, growth and proliferation. The groves and spikes structures additionally demonstrate photocatalytic activity, what was involved with presence of oxides on surfaces.

STUDY

In this work, the self-organised microstructures created using high-power femtosecond laser pulses are investigated. Three types of structures were obtained - spikes (A_1), grooves (A_2), and LIPSS (A_3) (Fig.1). The samples have been characterised by XRD, Raman spectroscopy, and scanning electron microscopy (SEM). The photocatalytic activity of the titanium surfaces produced was tested based on the degradation effect of methylene blue(MB). The correlation between the photocatalytic activity of TiO_2 coatings and their morphology and structure has been analysed. Features related to the size, shape, and distribution of the roughness patterns were found to influence the adhesion of the bacterial strain on different surfaces. On the laser-structured surface, the adhesion of *Escherichia coli* bacteria was reduced by 80% compared to an untreated reference surface (A_4).

Table 1. Laser process parameters

Sample	Energy per pulse, Ep (mJ)	Pulse frequency, (kHz)	Peak fluence, (J/cm²)	Step, (μm)	Polarisation	Scanning speed, V_s (m/s)
A_1	8	500	3.28	5	⊥	0.2
A_2	4	1000	1.64	10	⊥	0.8
A_3	1.95	1000	0.8	5	⊥	1
A_4	0	0	0	0	-	0

Table 2. The degradation kinetic parameters.

	$k_{app} \times 10^{-3}$[min^{-1}]	$t_{1/2}$ [min]
A_1	12.5	113.14
A_2	21.2	66.71
A_3 (LIPSS)	7.4	191.11
A_4 (polished)	6.9	204.96
Control (MB photolysis)	3.6	392.84

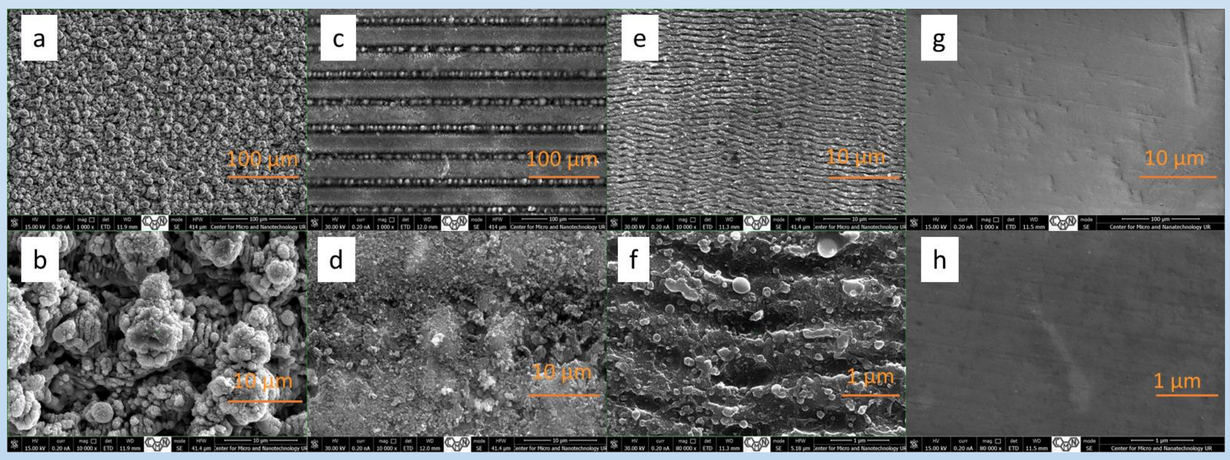

Figure 1. SEM images of structurised surfaces in different magnification of A_1 (a, b), A_2 (c, d), A_3 (e, f), A_4 (g, h)

An assessment of surface wettability was carried out by observing the behaviour of distilled water drops on the disc surface. All surfaces reveal a hydrophilic nature, with the contact angle values for samples 16.8 ± 1.8 (A_1), 44.1 ± 3.3 (A_2), 52.5 ± 7.5 (A_3) and 56.0 ± 1.4(A_4). The roughness of samples was established on the base of S_a parameter - the arithmetical mean height which values decreased in the order: A_1 > A_2 > A_3 > A_4. The Raman spectra of A_1 and A_2 samples contained lines characteristic of rutile and anatase TiO_2 forms. Semiquantitative analyses of phase content (rutile, anatase) were 73% rutile and 27% of anatase for A_1 and 38% and 62% for A_2. The photocatalytic activity of A_1 and A_2 may be associated with its phase composition (Table 1). Bacterial adhesion to the surface depends on both bacterial factors and surface properties. *E. coli* is a Gram-negative bacteria, of which the cell wall is composed of a thin layer of peptidoglycan and an outer membrane containing oligosaccharides, which gives the hydrophilic surface of it. Surfaces A_1 and A_2 contain an oxide layer, which causes them to have a surface charge in aqueous solution. A decrease in the number of bacteria cells was observed for the A_1, A_2, and A_3 discs, compared to the unstructured Ti disc, A_4 (Fig. 2A). For each of the modified Ti discs, a reduction in cell population (range between 79 and 87%) was observed.

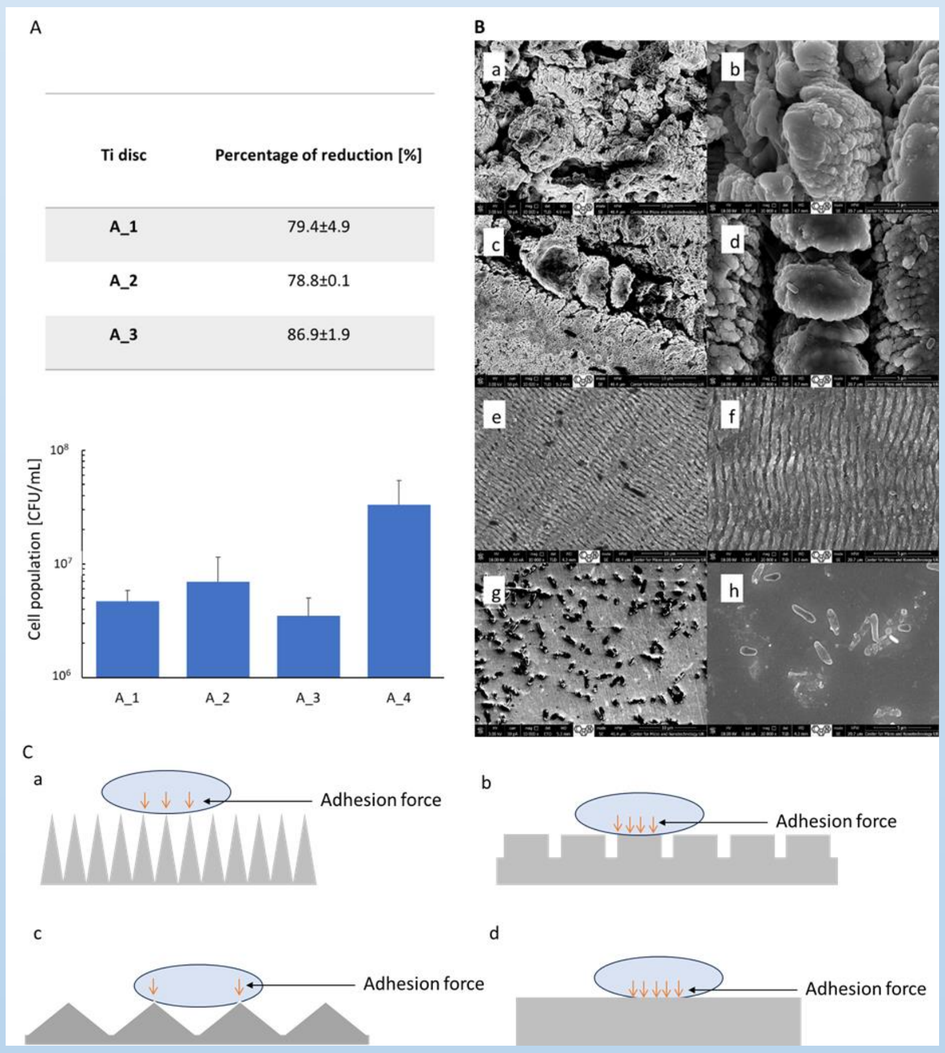

Figure 2. (**A**) The antibacterial activity of various titanium discs is shown as the number of CFU and percentage reduction in the cell population. The error bars indicated the standard deviation of two independent experiments, the statistical analysis was performed with Dunett´s multiple comparison test with GraphPad Prism. (**B**) SEM images of *E. coli* bacteria cells on surfaces A_1 (a), A_2 (c), A_3 (e), A_4 (g) (before Au spraying), A_1 (b), A_2 (d), A_3 (f), A_4 (h) (after Au spraying). (**C**) Schematic diagram of the bacteria-Surface interaction—A_1 (a), A_2 (b), A_3 (c), A_4 (d)

SUMMARY

Femtosecond-laser processing of Ti surfaces is a convenient single-step process of surface texturing that enables the generation of various patterns depending on used laser parameters. Depending on the laser parameters, the obtained structures differ in roughness, wettability, chemical composition, photocatalytic activity, and antibacterial properties. Modification of the surface with a femtosecond laser with pulse energy values of 4 and 8 mJ promotes the formation of titanium oxides on the surface. Surfaces containing an oxide layer showed photocatalytic activity. The LIPSS structures showed excellent properties in inhibiting *E. coli* adhesion. However, the remaining structures also have very good antimicrobial properties and additionally demonstrate photocatalytic activity.

Reference:
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