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Rapid hierarchical structuring of titanium surface by modulated fiber laser: Protecting the native surface chemistry

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ABSTRACT

Sand blasting and acid etching are the most common methods used to increase the roughness of orthopedic and dental implants for better osseointegration. However, possible process related contaminations remaining from these methods may cause an uncertainty if the cells are responding to the surface roughness or to the chemical residues. On the other hand, since it is clear that the presence of top native oxide layer of Ti implants is the primary step for better osseointegration, it is necessary to modify the surfaces residue free where the lasers can be the solution. In this respect, commercially pure Ti samples were structured with hierarchical micro and nano features by using modulated microsecond pulsed fiber laser while the surface is protected to its native chemistry. Surfaces were analyzed for their chemistries, roughness and wetting properties prior and subsequent to the structuring process.

1. Introduction

Titanium (Ti) and its alloys are the most favorite materials used at orthopedic and dental implants since their success lies behind their favorable interaction mechanisms with osteoblast cells where the passivated outer titanium dioxide (TiO_2) layer plays the major role [1–5].

In the literature, presence of oxide layer is pointed out as one of the most important parameter for enhanced biocompatibility of mostly used orthopedic and dental implants. It has been known that the naturally formed TiO_2 layer over Ti implants enhances the osseointegration [5]. Similar to Ti, alumina (Al_2O_3) is another native oxide material used for total hip prosthesis and dental implants, which reflects similar surface energies to Ti native oxide. It shows high biocompatibility mainly for osteoblast cell and for many others especially when prepared in nano scale [4,6–10]. Instead of using Ti/Ti alloys and alumina as they are, deposition of these materials to other biocompatible materials, such as PEEK, is also suggested for enhanced biocompatibility of these kind of materials [10,11].

On the other hand, suitable surface chemistry alone is not the solution for aseptic loosening, which is one of the main problem that the patients mostly suffer from. In order to overcome this problem, it has been suggested to enhance the implant surfaces via different treatment techniques, such as: surface roughening via sand blasting and acid etching [3,12,13]. It has been known that the increased surface roughness of Ti surfaces enhances the osteoblast anchorage and the alkaline phosphatase (ALP) activity [13,14]. However, possible process related contaminations at the top surface of implant remaining from the mentioned techniques above may cause a conflict whether the cell-surface interaction is influenced from the material surface or the contaminations [12,13,15]. This uncertainty may be cured by lasers.

Laser surface modification is one of the key methods for surface enhancement since it provides rapid modification of the surfaces with precise and repeatable results with and without influencing the surface chemistry [14–17]. Chikarakara et al. pointed out enhanced viability and attachment of pre-osteoblast cells on $TiAl_6V_4$ surface where the material surface is melt by pulsed CO_2 laser under Argon (Ar) gas flow to protect the surface from further oxidation [17]. May et al. highlighted in their research that it is possible to control one of the most important parameter controlling the cell-surface interaction, which is the surface wettability, via surface nitriding by pulsed laser structuring process under nitrogen gas flow [16].

In this respect, surfaces of commercially pure Grade-2 (CP-Gr2) Ti substrates were structured by using modulated microsecond pulsed fiber laser under Ar gas flow at both micro and nano scale, hierarchically. This was inspired from the natural structure of bone [18]. Structured surfaces were analyzed for their topographies, wetting properties and chemistries.

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2. Materials and methods

2.1. Preparation of Ti Substrates

1 mm thick CP-Gr2 Ti plates were polished prior to the cutting and structuring processes. In order to obtain mirror-like surface finish, Ti plates were mechanically polished by using P600, P1000, P2000, P2500 silicon carbide polishing papers and with 5 µm and 1 µm alumina powders, respectively. Samples were cut to 15 mm of diameter using modulated microsecond pulsed fiber laser operating at 1080 nm (JK400FGSI laser, UK), which can operate at 50 kHz of pulse frequencies maximum.

2.2. Laser structuring of Ti substrates

Ti samples were ultrasonically cleaned in absolute ethanol prior to the laser structuring. Surfaces were structured to mesh-like distribution using the same laser. During the structuring process, laser beam was defocused to produce 70 µm of spot diameter over the surface and samples were scanned in two directions with the speed of 5 mm/s. Laser pulse length, operation frequency and peak power were fixed to 50 µs, 4 kHz and 95.6 W, respectively. Laser system equipped with 6 mm of output diameter co-axial nozzle for the continuous flow of Ar gas, which helps cooling process, covers the structured area during the cooling cycle and prevents instantaneous oxidation process before re-solidification of structured region. Subsequent to structuring process, extra UV ozone cleaning procedure (Jelight Company Inc, USA) was applied to all samples in order to remove any possible organic contaminant. One set of polished Ti samples were excluded as blank.

2.3. Surface characterization

Scanning electron microscopy (SEM) (XL30 ESEM, Philips Corporation, Netherland) was used in order to characterize the surface topography of the multi-scale structured Ti surfaces. Working distance of SEM was kept constant during the examination.

Chemical analyses of the Ti surfaces before and after laser structuring under Ar shielding gas were performed by X-Ray photoelectron spectroscopy (XPS), which uses Al-Kα source gun (KAlpha+ X-ray Photoelectron Spectrometer, Thermo Scientific, USA).

Roughness properties of the surfaces were analyzed by using whitelight interferometer (NewView 7200, Zygo Corporation, USA) and atomic force microscope (AFM) (Ambios Quesant Q-Scope Universal SPM, USA). Tapping mode was selected for AFM analysis. Average roughness values were calculated from three randomly selected locations.

Wetting properties of the substrates were measured by CAM-100 contact angle meter (KSV Instruments, Finland) via static contact angle measurement technique after UV-Ozone cleaning. Six regular measurements were used to calculate the average contact angle value of the surfaces.

3. Results and discussion

Schematic drawing of designed co-axial nozzle system can be seen in Fig. 1a. SEM micrographs were shown in Fig. 1b, c, d and e. As can be seen from the Fig. 1b Ti surface was successfully structured to a mesh-like distribution by applied laser pulses, which created microscale secondary structures as a result of laser repetition rate. Width of the generated mesh line was measured as 90 µm and the period of the structures were measured as 180 µm as they were defined previously. As it can be seen at the high magnification images, nanoparticles were formed over the micropatterns (microstructures) (Fig. 1c and d), and also over the intermediate region (Fig. 1e) as a result of ablation process, which is actually indirect processing [15,19]. Here, the Ar gas flow assisted the formation of these nanoparticles. Size of the nanoparticles were measured as 24.0 ± 5.0 nm in diameter as published before [15].

In order to examine if the surface chemistry changes after laser processing, Ti-2p shell XPS analysis were performed to non-structured and laser-structured Ti samples. Obtained results are given in Fig. 2. As can be seen in Fig. 2a, characteristic peaks of TiO_2 layer were recorded at 458.20 eV, 458.70 eV, 459.60 eV and

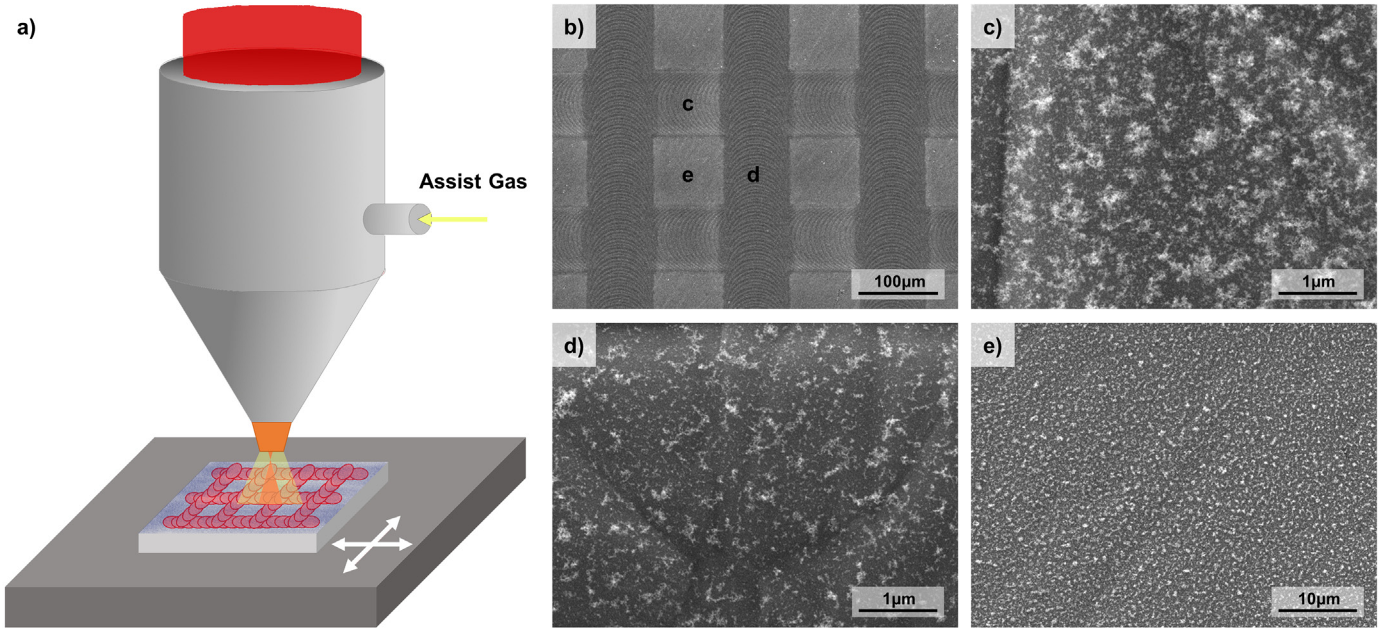

Fig. 1. a) Schematic illustration of laser surface structuring under Ar gas flow with co-axial nozzle. b) SEM micrograph of mesh like structure realized by microsecond laser pulses. High magnification SEM micrographs of regions indicated as "c and d" in "b)", which are the c) first scan and d) the second scan, of structuring process. e) High magnification image of intermediate region indicated as "e" in "b)" where the laser did not alter the surface.

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