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Multi-scaled femtosecond laser structuring of stationary titanium surfaces

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The evolution of the topography of titanium surfaces treated with femtosecond laser radiation in stationary conditions as a function of radiation fluence and number of laser pulses is investigated. Depending on the processing parameters, ripples, microcolumns, wavy or smooth surfaces can be obtained. The ripples predominate for fluences near the damage threshold of titanium (0.2±0.1) J/cm², while microcolumns form during the first 200 pulses for fluences between (0.6±0.2) and (1.7±0.2) J/cm^2. A wavy topography develops for fluences and number of pulses higher than (1.7±0.2) J/cm^2 and 300, respectively. A bimodal surface topography consisting of surface ripples overlapping a microcolumnar topography can be obtained if the surfaces are firstly treated to create microcolumns followed by laser treatment with a lower fluence near the ablation threshold of the material, in order to generate periodic ripples.

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1. Introduction

The formation of a pattern of microcolumns on solids irradiated with femtosecond laser pulses has been reported for a wide range of materials including metals, semiconductors, ceramics and polymers [1-5]. The morphology of these microcolumns depends on the processing parameters, such as the number of incident laser pulses, radiation fluence, laser beam wavelength, pulse duration, composition and pressure of the ambient atmosphere, and the relative velocity between the sample and the laser beam. For titanium, cumulative irradiation effect with femtosecond laser pulses can produce a large variety of surface structures. For instance, nanoprotusions with a size down to 20 nm, ripples with a periodicity at the sub-micron level, microcolumns with dimensions in the range of 1-15 μm, nanostructured microcolumns, smooth surfaces with micro-inhomogeneities, and smooth surfaces with sphere-like nanostructures down to 10 nm have all been observed [6-8]. Since textured titanium surfaces enhance endosseous implants performance, such as protein absorption, osseointegration and strength of the bone/implant interface [9-11], laser textured surfaces may yield interesting properties for biomedical applications.

In a previous work [12] we have compared the surface topography of stationary and non stationary titanium samples irradiated by femtosecond laser radiation at average fluences near 1 J/cm². In both cases, a microcolumnar surface texture was formed in the center of the irradiated areas, while ripples were formed in the periphery of these areas. When experiments were performed with non-stationary samples, the microcolumns showed a peculiar characteristic: they exhibit ripples similar to those observed at the periphery of the treated areas. Since the energy distribution in the transverse cross section of the laser beam is Gaussian, we concluded that the ripples were formed when the microcolumns are submitted to fluences near the ablation threshold of the material, at the trailing edge of the moving laser beam.

In the present work, the evolution of microcolumns formed on titanium surfaces in stationary treatment conditions as a function of the radiation fluence and the number of laser pulses is studied. The obtained results show that microcolumns are generated in a limited fluence range and for well defined number of laser pulses. The possibility of creating a bimodal surface topography consisting of surface ripples overlapping microcolumns similar to those previously observed in non-stationary experiments was investigated.

2. Experimental

A commercial Yb:KYW chirped-pulse-regenerative amplification laser system (Amplitude Systemes s-pulse HP) is used to provide s-polarized lasers pulses with a duration of about 500 fs at a central wavelength of 1030 nm. Laser processing was performed in air on metallurgically polished grade 2 biomedical titanium samples typically used in low load bearing medical devices, such as dental implants and osseointegration plates. The laser beam was kept stationary and focused perpendicularly to the sample surface using a 100 mm focal-length lens. The pulse energy was measured using a powermeter and varied between 0 and 1 mJ by means of an energy attenuator. The pulse repetition rate was maintained at 10 Hz. For the nanostructuring experiments, a half wave plate was used to control the polarization direction of the laser beam**.** After the laser treatment, the achieved surface topography was characterized by scanning electron microscopy (SEM).

3. Results and discussion

3.1 Effect of radiation fluence

The evolution of the surface topography of titanium samples treated with different pulse energies is depicted in figure 1. Since the laser beam is approximately Gaussian, the spatial fluence profile for each spot $F(r)$ is given by:

$$F(r)=\frac{2E}{\pi w_0^2}e^{-2\frac{r^2}{w_0^2}} \tag{1}$$

where w_0 is the beam radius defined as the distance from the beam axis where the fluence drops to $1/e^2$ of the peak value, and r is the distance from the beam axis. The parameter w_0 can be determined from the diameter of the regions affected by the laser treatment and the value of the ablation threshold of titanium [13]. Since the ablation threshold of titanium for the radiation wavelength and processing conditions used in the present work is unknown, a slightly different approach was adopted. From Fi.g. 1, one can observe that microcolumns are formed for pulses with average energies higher than 44 μJ and that the radii of the areas where microcolumns form increases with increasing pulse energy. As a result, if r_1 and r_2 are the radii of the microcolumns areas for energies E_1 and E_2, the threshold fluence for microcolumns formation can be calculated from:

$$F_{threshold}=F(r_1)=F(r_2)=\frac{2E_1}{\pi w_0^2}e^{-2\frac{r_1^2}{w_0^2}}=\frac{2E_2}{\pi w_0^2}e^{-2\frac{r_2^2}{w_0^2}} \tag{2}$$

Since the distance between the lens and the samples surface is kept constant in all experiments and the pulse energy is controlled by a beam attenuator, the beam radius w_0 is independent of the pulse energy. As a result, w_0 can be found using the equation:

$$w_0=\sqrt{\frac{2\left(r_1^2-r_2^2\right)}{\ln E_1/E_2}} \tag{3}$$

From the micrographs of Fig. 1 an average value of $w_0=(105\pm 25)\mu m$ was obtained for the laser beam radius. Using this value, the ablation threshold of titanium was estimated at (0.2±0.1) J/cm², the microcolumns formation threshold at (0.6±0.2) J/cm², and the maximum fluence for which microcolumns are still formed at (1.7±0.2) J/cm².

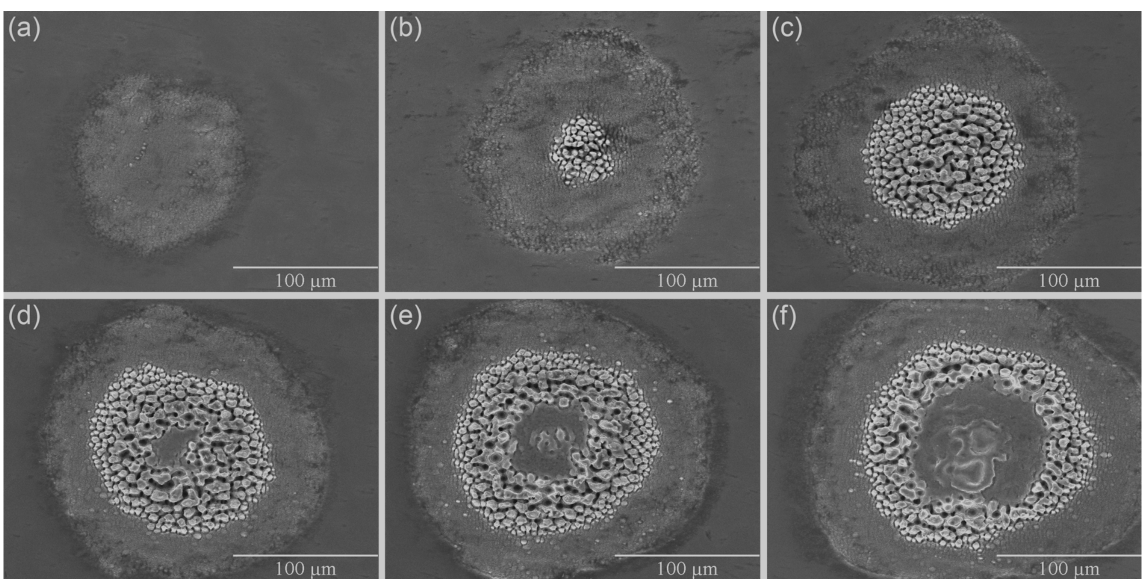

Fig. 1. SEM micrographs of titanium surfaces treated with 200 laser pulses at (a) 44; (b) 86; (c) 176; (d) 262; (e) 340; and (f) 518 μJ.

Larger magnification of the micrographs of some of the treated surfaces presented in figure 1, and the corresponding laser fluence spatial distribution calculated from eq. (1) are presented in figure 2. For the lowest pulse energy used (figure 2a and 2d) the maximum fluence is about 0.25 J/cm². As a result, no microcolumns are formed in the treated region. Instead, ripples are observed at its periphery, where fluence is close to the ablation threshold of the material, and a smooth surface is formed in the central areas of the spot. If the average energy is increased to 86 μJ (figure 2b and 2e), microcolumns appear at the centre of the treated area, where the maximum fluence exceeds the threshold for microcolumn formation. At 262 μJ (figure 2c and 2f), three regions can be distinguished as one goes from the centre to the periphery of the treated area. At the centre a small flat region exists where microcolumns did not form because the radiation fluence was higher than the upper limit for microcolumns formation (1.7±0.2) J/cm². Microcolumns are observed in an annular region when the fluence is in the range 0.6 to 1.7 J/cm². Finally, at the periphery of the treated area only ripples are observed.

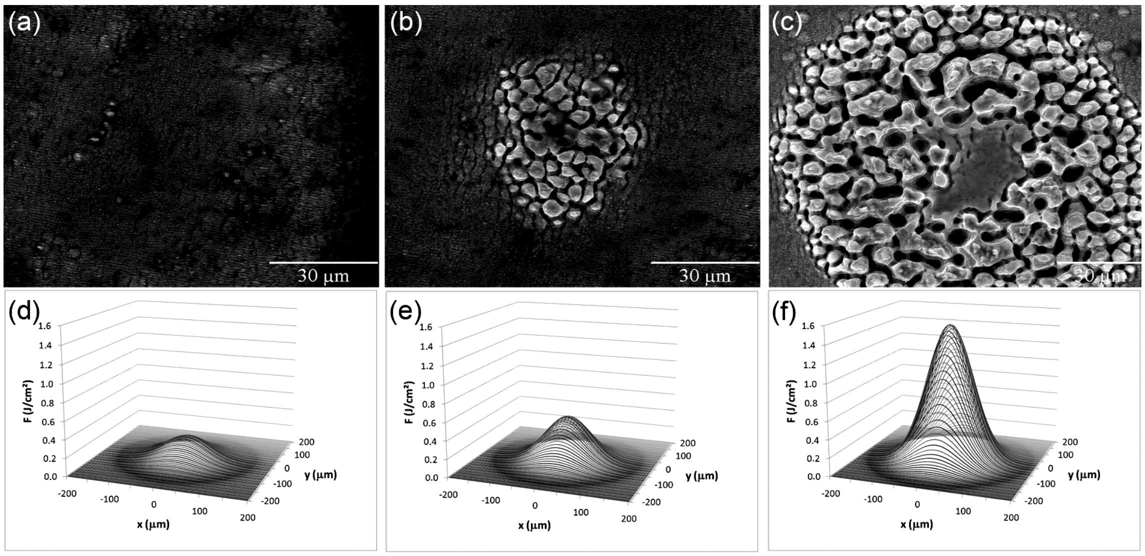

Fig. 2. SEM micrographs and corresponding laser fluence spatial distribution of titanium surfaces treated with average energy of: (a) and (d) 44 μJ; (b) and (e) 86 μJ; and (c) and (f) 262 μJ.

3.2 Effect of the number of laser pulses

The evolution of the surface topography with increasing number of pulses is depicted in Fig. 3. The first ten pulses lead to the formation of small depressions and hillocks randomly distributed in an external annular region of the treated area (Fig. 3a). With increasing number of pulses, these defects evolve to droplets (Fig. 3b) and eventually to microcolumns (Fig. 3c). In the center of the annular region no microcolumns are observed at this point, and the surface is relatively smooth. In contrast, after 300 laser pulses, a curious change is observed as a wavy topography starts to develop in the central region of the treated area (Fig. 3d). With a further increase of the number of pulses (Fig. 3d and 3e), the dimensions of the waves increase while microcolumn development seems to stagnate.

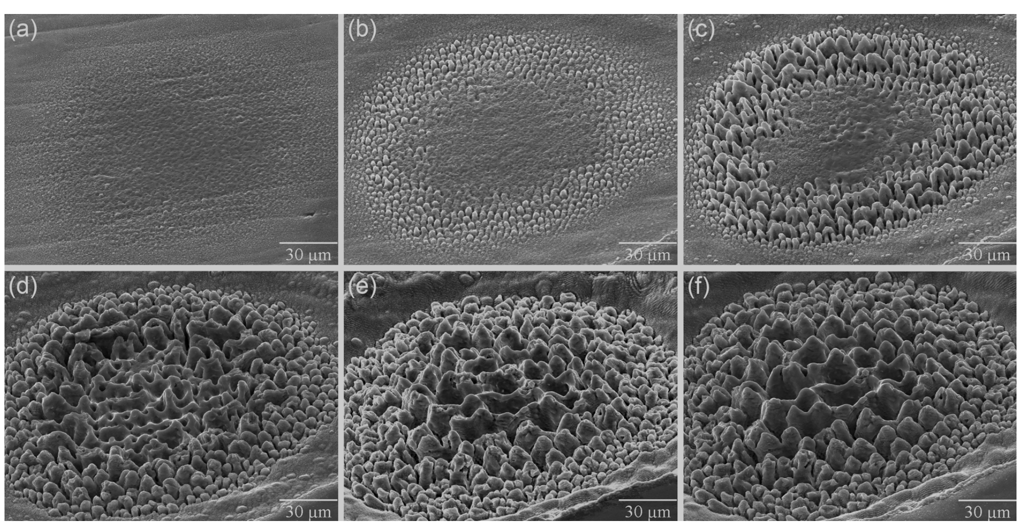

Fig. 3. SEM micrographs of titanium surfaces treated with average energy of 518 μJ and (a) 10; (b) 50; (c) 100; (d) 300; (e) 500; and (f) 1000 pulses. The samples were tilted 45°.

3.3 Nanostructuring of microcolumnar surfaces

In a previous publication [12], we showed that it is possible to obtain a bimodal surface topography consisting of nanostructured surface microcolumns when the laser treatment is performed with relative motion between the laser beam and the sample. A similar bimodal surface topography can also be obtained using stationary titanium samples. In order to obtain this topography, samples are first treated with fluences in the range where microcolumns form (figure 4a and 4b). In a second step, the laser treated area is irradiated again with fluences near the ablation threshold of titanium in order to generate only ripples. As a result, the surface of the microcolumns is covered with nanosized periodic ripples (figure 4c and 4d). By changing the direction of the beam polarization the orientation of the ripples can be controlled and microcolumns nanostructured in different directions obtained (figure 4e and 4f). Interestingly, a dot-like nanostructure can also be overlapped to the microcolumns when the polarization direction of the laser beam is changed by 90° during the same laser treatment (figure 4g and 4h).

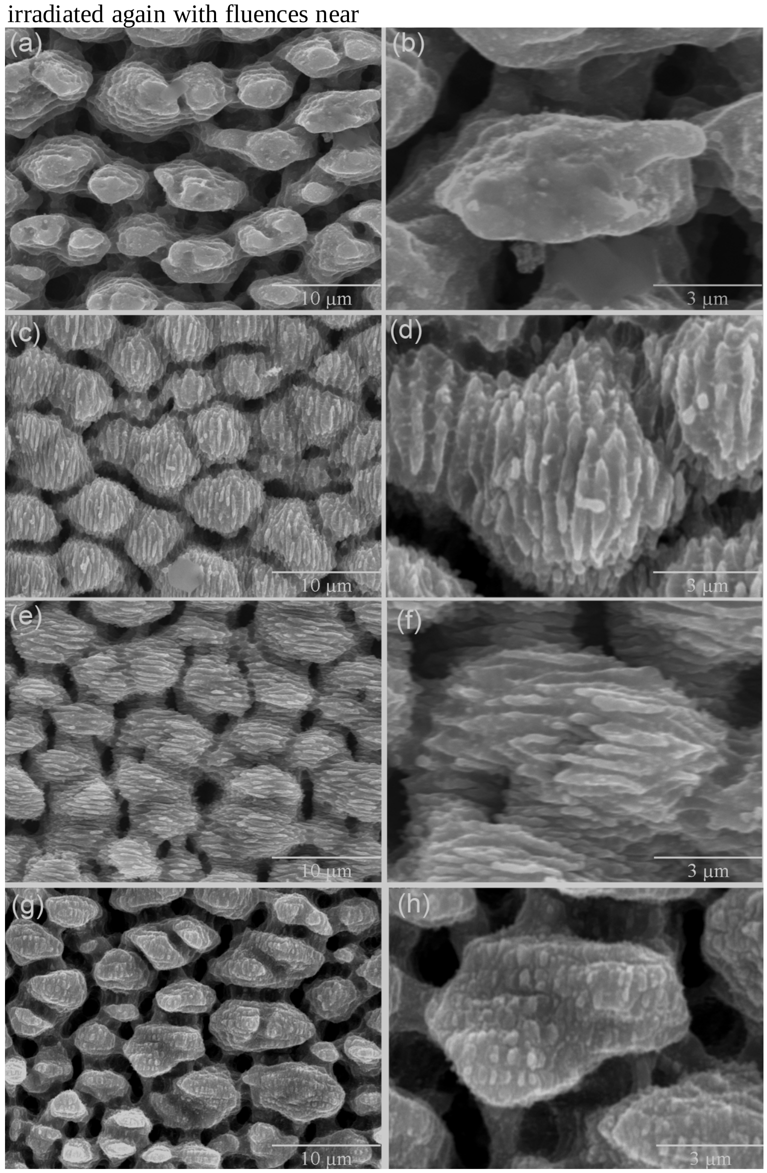

Fig. 4. SEM micrographs of the: (a) and (b) microcolumns produced with 200 laser pulses at 518 μJ; (c), (d), (e) and (f) vertically and horizontally nanostructured microcolumns produced with 200 laser pulses at 518 μJ combined with 20 laser pulses at 44 μJ; (g) and (h) dot-like nanostructured microcolumns produced by a 90° change in the direction of the beam polarization during the laser treatment with 20 laser pulses at 44 μJ.

4. Discussion

Periodic ripples similar to those observed in figure 2a have been previously observed in several materials processed with femtosecond laser radiation at fluences just above the material damage threshold [14-15]. The most consensual explanation for their formation is that they originate from an inhomogeneous energy distribution due to the interference of the incident laser beam with scattered radiation, for example, by microscopic asperities of the surface, propagating parallel to the surface [16-17]. The ripples formed by this mechanism are perpendicular to the electric field vector of the incident laser beam and their period is similar to the radiation wavelength. In the present work, ripples with a spatial periodicity of about 700 nm are observed at the periphery of the treated area where the radiation intensity is lower. The ripples period is appreciably less than the laser radiation wavelength (1030 nm). This discrepancy may be explained by an increase of the real part of the material refraction index due to the development of nanostructures during the first laser pulses [18].

Microcolumns develop during the first 200 pulses for fluences between (0.6±0.2) and (1.7±0.2) J/cm^2. The qualitative features of microcolumns evolution with the number of pulses are the same as previously reported in [12]: small depressions and hillocks formed during the first pulses evolve to droplets, and, eventually, to microcolumns with increasing number of pulses. Since the microcolumns protrude above the untreated surface, they cannot be formed by a preferential etching mechanism, as it is the case of the well-known cone-shaped structures that develop in polymers and other materials [19-20]. Instead, columns seem to grow through a hydrodynamical process similar to that reported for silicon treated with nanosecond laser pulses [21]. When the fluence exceeds (1.7±0.2) J/cm^2, the treated surfaces remain flat except for samples treated with 518 μJ and more than 200 pulses. For these samples a curious change was observed as a wavy topography develops in the central region of the treated area. The origin of these waves requires further investigation. One possible explanation may be the formation of capillary waves on the surface of molten titanium, as previously suggested to explain their formation in metals [21].

The wide range of surface textures that can be achieved, the characteristics of these textures and the controllability of the texturing process suggest that femtosecond laser are promising tools for surface texturing of endosseous implants but *in-vitro* and/or *in-vivo* investigations must be performed in order to evaluate their potential for biomedical applications.

5. Conclusions

Depending on the processing parameters, ripples, microcolumns, wavy or smooth surfaces can be obtained by surface texturing of titanium using a femtosecond pulse duration laser. The ripples predominate for fluences near the ablation threshold of titanium while microcolumns form for fluences between (0.6±0.2) and (1.7±0.2) J/cm^2. A wavy topography develops for fluences and number of pulses higher then (1.7±0.2) J/cm^2 and 300, respectively. Well-oriented periodic ripples can be overlapped to the microcolumns using a two-step processing. The ripples orientation can be precisely controlled by changing the polarization direction of the laser beam.

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