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Surface morphology modifications of titanium based implant induced by 40 picosecond laser pulses at 266 nm

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ABSTRACT

Surface modification of titanium based implant Ti6Al4V induced by an Nd:YAG laser operating at a wavelength of 266 nm, with pulses of 40 ps, is presented. It is shown that the laser beam at fluences 0.96 J cm^{-2} and 0.29 J cm^{-2} significantly modifies the alloy surface. The damage threshold is estimated at 0.12 J cm^{-2}. The irradiations at 0.96 J cm^{-2} were accompanied by the occurrence of plasma. The characteristics of the damage are: (a) smoothed center of the damage area, (b) 20 nm cracks, (c) 200 nm parallel periodic surface structures (PSS). The periodicity of the PSS corresponds to the laser wavelength. Such modifications of the Ti6Al4V implant surface are applicable to medical practice. Surface morphology of the implant was monitored by optical microscopy (OM) and scanning electron microscopy (SEM) coupled to an energy dispersive spectroscopy (EDS) analyzer.

1. Introduction

Titanium and its alloys are materials with applications varying from biomedical and aerospace technology to crucial components of nuclear fusion reactors [1–6]. They are also used in power production, chemical processing, and computer industry (titanium is a promising substrate for hard disk drives) [7]. Titanium materials are inert to body fluids, do not react with tissue, and therefore cause no infection in the body. They also have the ability to bind with the living tissue and to the bones, and are thus widely spread biomaterials [4,8].

The most widely used Ti-alloy is the Ti6Al4V (Ti6-4) $\alpha + \beta$ alloy, used for orthopaedic surgery implants (hip and knee), wrought screws and fittings, dental implants and pacemaker housings. An important aspect of biointegration is the surface morphology of the alloy (surface topography, surface charge density, surface free energy, and the composition of the material) [9,10]. In order to enhance the bone/implant integration of Ti-based materials, research is oriented towards laser assisted techniques of surface modification [11–15].

Surface modifications of materials by laser beams have long been an interest in various fields. Understanding the basic principles of coupling between laser radiation and surface [16] is necessary in developing industrial and medical applications of laser beams, both at low levels and high levels of impact, ranging from texturing to ablation [17–19]. Very often, accompanying processes and interactions with the plasma usually formed in front of the target [20] are as important, too.

Modifications of Ti-alloys by various microsecond and nanosecond pulse lasers (Nd:YAG, XeCl and KrF excimer, etc.) have been widely investigated [9–13,21–23]. To date, picosecond (ps) laser modification of these alloys has not been extensively reported in literature. It is important to establish conditions that allow various morphological modifications to occur, e.g. how the occurrence of the periodic surface structure depends on laser fluence. Such results are important in, e.g. Nd:YAG pulsed laser deposition of polymer thin films on Ti-alloy surface [24]. The pulsed Nd:YAG at 266 nm has particularly been found advantageous in surface texturing [25]. With the present work we extend our study on Ti6Al4V surface modifications to the ultraviolet laser wavelength of 266 nm, besides the wavelengths of 1064 nm and 532 nm, that we have reported earlier [26], all in the picosecond regime.

2. Experimental

The samples, flat plates with dimensions 15 mm × 10 mm × 0.5 mm (length × width × thickness), were made from a medical grade Ti6Al4V alloy, with chemical composition, by weight, Ti: 90%, Al: 6%, and V: 4%. The plates were

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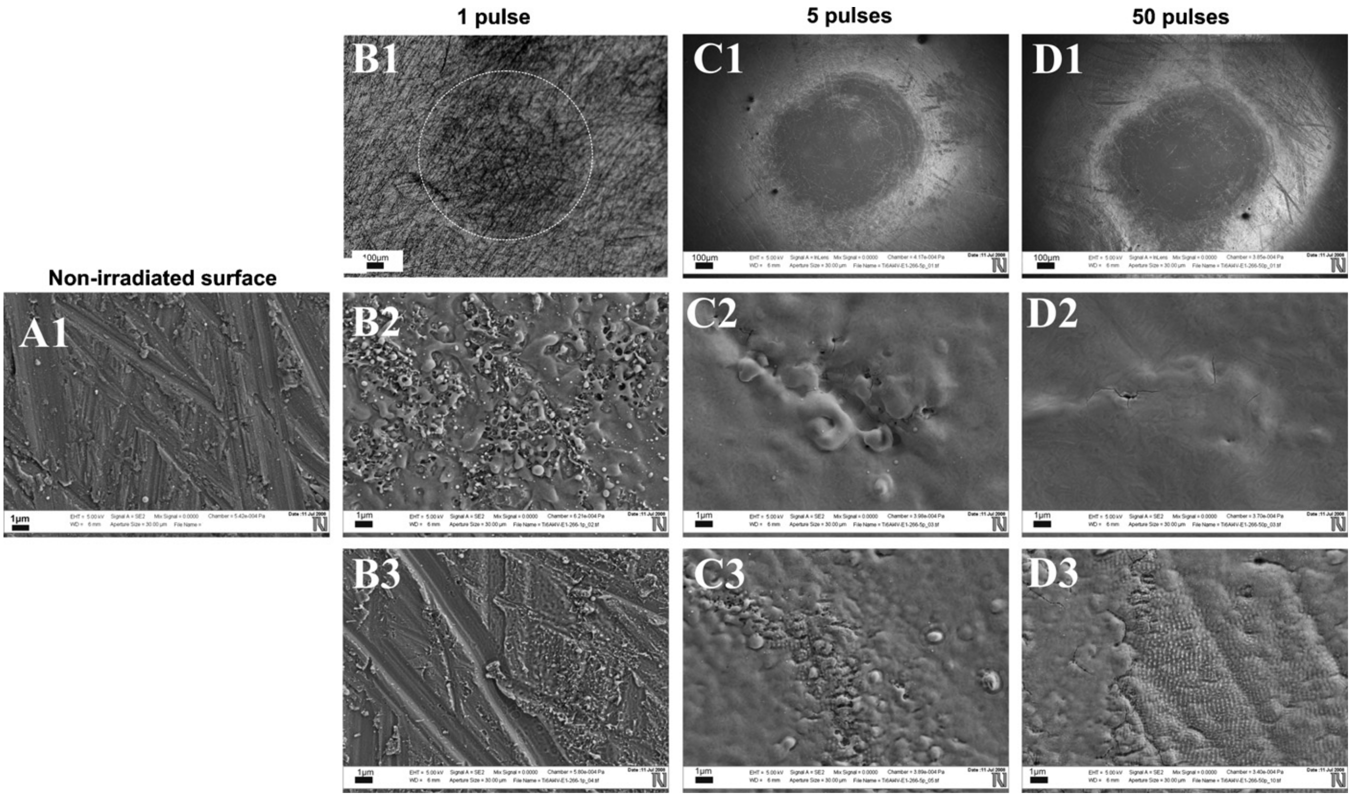

Fig. 1. Laser induced morphology modifications at a fluence of 0.96 J cm^{-2} recorded by SEM (except for B1, recorded by OM). (A1) The non-irradiated surface. (B) Ti6Al4V after 1 pulse: B1, entire spot; B2, detail from the center; B3, near periphery of the damage area. (C) Ti6Al4V after 5 pulses: C1, entire spot; C2, detail from the center; C3, periphery of the damage area. (D) Ti6Al4V after 50 pulses: D1, entire spot; D2, detail from the center; D3, near periphery of the damage area.

prepared by the standard procedure (cleaning, rinsing, etc.) and polished on the face-side.

The samples were irradiated by a Nd:YAG laser beam at a wavelength of 266 nm and 40 ps pulse. The laser was an active–passive mode-locked Nd:YAG system [27], model SYL P2 produced by QuantaSystem Srl.-Solbiate. It includes a laser oscillator, an amplifier and a non-linear crystal (KD × P). The laser was operated in TEM_{00} mode with a typical repetition rate of 2 Hz. The angle of incidence of the beam with respect to the sample surface was 90°. All surface irradiations were performed under ambient conditions. The results presented below are obtained at two laser fluences reaching the target: 0.96 J cm^{-2} and 0.29 J cm^{-2} and the effects observed with increasing pulse count. Laser fluence at the target was varied by means of neutral density filters.

Surface morphology and surface chemical compositions of the irradiated and non-irradiated areas were analyzed by optical microscopy (OM), scanning electron microscopy (SEM, JOEL-JSM-6500F) and energy dispersive spectroscopy (EDS) analysis. The reflectance spectrum of the Ti6Al4V surface was recorded by a Perkin Elmer Lambda 35 UV–vis spectrophotometer in the wavelength range from 190 to 1100 nm. Profilometry was used to investigate the geometry of the damage area.

3. Results and discussion

In metals, laser light is generally absorbed by electron plasma/free electrons, and the energy is passed onto the lattice, producing morphological modifications. These modifications generally depend on laser wavelength, fluence, pulse duration, repetition rate, number of accumulated pulses, etc. In the present case, with the fixed laser wavelength and pulse duration, they depended on laser fluence and the number of applied pulses, at energies above the damage threshold.

No crater formation was detected by profilometry, only irregular microroughness produced by melting and solidifying. The main effects produced by the laser pulses were cracks, microroughness (on the order of microns) and periodic surface structures (PSS). The average width of the cracks was 20 nm. The damage threshold laser fluence was estimated at 0.12 J cm^{-2} in a procedure recommended for pulses longer than 10 ps [28]. As in previous work [26], the threshold was determined as an average from several spots on the surface, taking care that smoother parts of the surface are chosen, given its non-ideal state. The periodic surface structures (PSS) showed a periodicity of 200 nm, which corresponded to the laser beam wavelength. The impact spots and surface morphology features produced by laser pulses at the fluence of 0.96 J cm^{-2} are presented in Fig. 1, together with the image of the non-irradiated

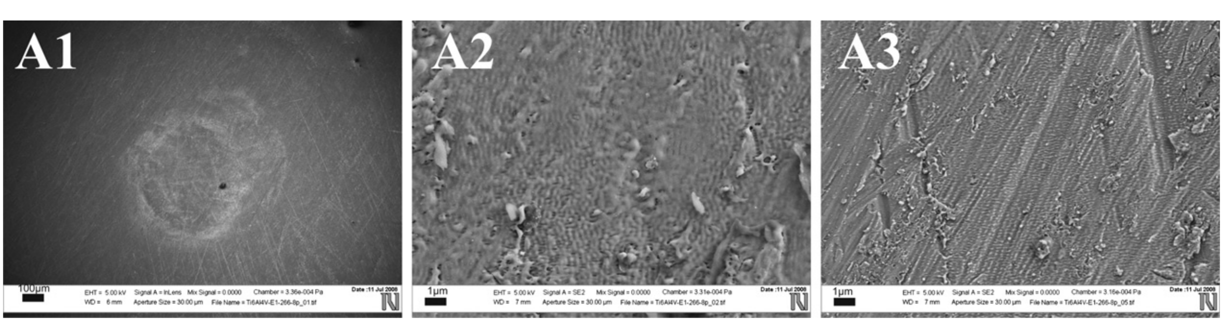

Fig. 2. Ti6Al4V after 8 pulses at a fluence of 0.29 J cm^{-2}: A1, entire spot; A2, detail from the center; A3, near periphery of the damage area.

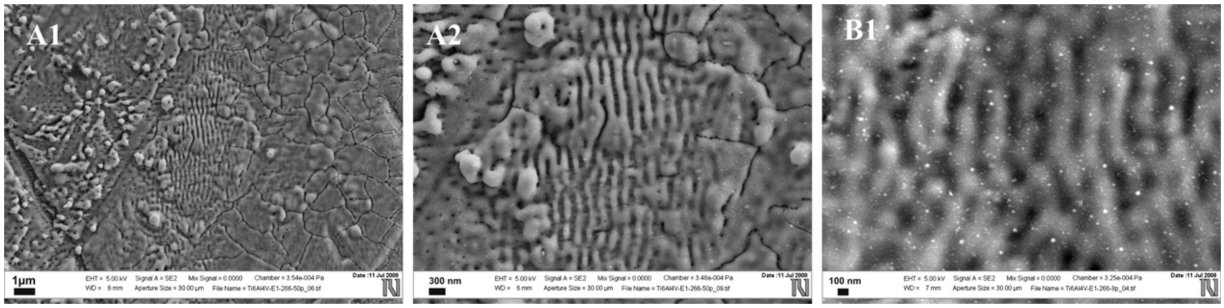

Fig. 3. SEM views of periodic surface structures formed at both fluencies. At 0.96 J cm^{-2} the periphery of the damaged area after 50 pulses, at lower magnification (A1) and higher magnification (A2). At 0.29 J cm^{-2}, 8 pulses, center of the damage area (B1).

surface (Fig. 1-A1). The figure contains SEM images of the spots resulting from different pulse counts (columns in Fig. 1). The images also present three different views of the spots: general view, central area, and peripheral area (rows in Fig. 1). In the same manner, the spots produced by the laser fluence of 0.29 J cm^{-2} are presented in Fig. 2.

The result of the application of a single pulse was microroughness (micrometer size roughness) at the center of the damage area (Fig. 1-B2). Fig. 1-C2 and D2 shows that the surface melts and becomes significantly smoother with increasing number of accumulated laser pulses. Apparently, the laser fluence was too low to induce thermal expansion or any other effect that would lead to formation of craters. However, the 266 nm light is sufficiently absorbed by the Ti6Al4V material, so that melting occurs. Also, after 5 laser pulses or more, characteristic surface features are cracks of 20 nm average width, which most likely result from the very high cooling rate of the melted area after irradiation [29]. The pulses at 0.96 J cm^{-2} were accompanied by occurrence of plasma in front of the target.

Fig. 2 presents surface modifications produced by the laser at the fluence of 0.29 J cm^{-2}, which is near the damage threshold. In this case, the center of the damage spot is relatively smoother, with no hydrodynamic effects, and surface periodic structures and microroughness appear in the center, instead of the periphery (Fig. 2-A2).

Particularly interesting features generated after irradiating the Ti6Al4V are periodic surface structures (PSS). It was shown in our previous study that the periodicity of the PSS on this material depends on the wavelength [26]. Fig. 3 shows these structures after irradiation of the 266 nm laser at both fluences used here. The structures have the form of parallel ripples, perpendicular to the laser electric field vector. The periodicity of the structures obtained by either of the fluences is about 200 nm, which is in accordance with the laser wavelength of 266 nm. At the fluence of 0.96 J cm^{-2} the structures appear after about 10 pulses, at the periphery of the damage area. At the fluence of 0.29 J cm^{-2} the structures also appear after 8 pulses, but at the center of the damage area (B1). Periodic surface structures are generally formed by low intensity laser beams. Therefore, after 50 pulses with 0.96 J cm^{-2}, the center is molten, and the PSS are formed at the periphery. Accordingly, with the lower fluence of 0.29 J cm^{-2} the PSS are formed at the center.

The damage threshold of 0.12 J cm^{-2} found with the present laser wavelength of 266 nm is quite low compared to the thresholds found with longer wavelengths of the same laser, determined in the same way (0.25 J cm^{-2} and 0.9 J cm^{-2}). In order to understand some of the reasons for this, we recorded a reflectance spectrum of the Ti6Al4V material by a Lambda 9, Perkin Elmer, UV-VIS-NIR spectrophotometer. The spectrum is presented in Fig. 4.

The reflectance spectrum shows that the light reflectance off the Ti6Al4V surface drops by a factor of two from 1064 nm to 266 nm. This implies that the absorption of the 266 nm light by Ti6Al4V is two times higher than the absorption at 1064 nm. It is certainly one of the reasons why it takes significantly lower laser fluencies to damage the surface of Ti6Al4V at 266 nm.

EDS analysis showed no measurable oxidation as the result of the laser action at 266 nm, nor change of chemical composition in the damage area (it remained in the ratio Ti:Al:V = 90:6:4 within a half percent range).

It is important to note that none of the features of these structures indicates imprinting of a diffraction pattern originating from the optical system of the laser source, which can thus be excluded [30,31].

A comparison of damage thresholds and PSS effects produced by the 266 nm Nd:YAG laser with previously reported results obtained with the 1064 nm and 532 nm Nd:YAG laser is given in Table 1. The damage thresholds are apparently well associated with reflectance properties of the material at corresponding wavelengths: they are lower for lower reflectance.

The absence of craters (confirmed by profilometry, not shown here) in the 266 nm case is probably due to the low fluence used, but a possible shielding effect should not be neglected in the case of the shorter laser wavelength, by the plasma formed at the beginning of each pulse [26]. However, it apparently takes less energy to induce initial damage at this short wavelength (low damage threshold), but the plasma that is formed shields the target later on in the pulse, and prevents crater formation.

It is important to note that the periodicity of the PSS changes in a very consistent and regular manner with the wavelength of the laser: it drops by a factor of two, each time the laser wavelength is lowered by the same factor (Table 1).

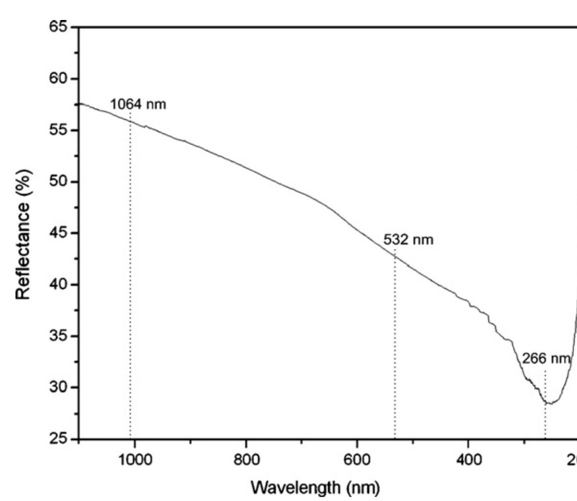

Fig. 4. Reflectance spectrum of the non-irradiated Ti6Al4V surface, with laser wavelengths indicated.

Table 1
A comparative sum-up of effects produced by the three laser wavelengths.

	Reflection	Damage threshold	Periodic surface structures
Laser at 1064 nm [26]	57.00%	0.9 J cm^{-2}	Nanometer scale; parallel waves, ⊥ to $\vec{E}$ period: 800 nm after 30 pulses
Laser at 532 nm [26]	42.70%	0.25 J cm^{-2}	Nanometer scale; parallel waves, ⊥ to $\vec{E}$ period: 400 nm after 50 pulses
Laser at 266 nm	29.00%	0.12 J cm^{-2}	Nanometer scale; parallel waves, ⊥ to $\vec{E}$ period: 200 nm after 8 pulses

4. Conclusion

The Ti6Al4V titanium medical grade alloy was irradiated by 40 ps pulses of a Nd:YAG laser at a wavelength of 266 nm. The effects are compared to those obtained with the longer wavelengths of the same laser, 532 nm and 1064 nm, with the same pulse duration. The laser fluences used at the present wavelength, 0.96 J cm^{-2} and 0.29 J cm^{-2}, significantly modify the alloy surface. All the irradiations at 0.96 J cm^{-2} were accompanied by occurrence of plasma. The characteristics of the damage are: (a) smoothed center of the damage area due to melting, (b) 20 nm cracks, (c) 200 nm parallel periodic surface structures (PSS). The periodicity of the PSS corresponds to the laser wavelength in a very consistent manner, as supported by the previous results at longer wavelengths. No craters were observed, as should be expected due to the lower fluences available at the present wavelength, but possibly also coupled with the shielding effect of the plasma formed at the early stages of the pulse. The damage threshold of 0.12 J cm^{-2} found with this wavelength is the lowest of all three laser wavelengths mentioned, which is consistent with the lowest reflectance off the target surface found for it.

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