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Surface modification of the titanium implant using TEA CO_2 laser pulses in controllable gas atmospheres – Comparative study

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ABSTRACT

Interaction of a TEA CO_2 laser, operating at 10.6 μm wavelength and pulse duration of 100 ns (FWHM), with a titanium implant in various gas atmospheres was studied. The Ti implant surface modification was typically studied at the moderate laser beam energy density/fluence of 28 J/cm^2 in the surrounding of air, N_2, O_2 or He. The energy absorbed from the TEA CO_2 laser beam is partially converted to thermal energy, which generates a series of effects, such as melting, vaporization of the molten material, shock waves, etc. The following titanium implant surface changes and phenomena were observed, depending on the gas used: (i) creation of cone-like surface structures in the atmospheres of air, N_2 and O_2, and dominant micro-holes/pores in He ambient; (ii) hydrodynamic features, most prominent in air; (iii) formation of titanium nitride and titanium oxide layers, and (iv) occurrence of plasma in front of the implant. It can be concluded from this study that the reported laser fluence and gas ambiences can effectively be applied for enhancing the titanium implant roughness and creation of titanium oxides and nitrides on the strictly localized surface area. The appearance of plasma in front of the implants indicates relatively high temperatures created above the surface. This offers a sterilizing effect, facilitating contaminant-free conditions.

1. Introduction

Titanium shows excellent physical and chemical properties – high melting point, high strength-to-weight ratio, impressive corrosion and erosion resistance, etc. [1]. Due to these desirable characteristics the titanium is attractive for numerous applications nowadays, such as aero-space and marine engineering, medicine (artificial heart valves, surgical instruments, components of high-speed blood centrifuge), etc. Focusing on the medicine, titanium and titanium-based alloys are used as various implants. The reason for this is a high level of biocompatibility, since titanium is non-toxic and not rejected by the body [2–9]. Titanium implants are widely employed in orthopedic, dental area, etc. Titanium CP grade is superior compared to other implant materials like stainless steel or cobalt–chromium–molybdenum implants and shows long-term durability [2]. It is well known that the success of bio-integration with the surrounding host tissues depends on the efficiency of the cell/tissue-implant coupling [4,6,7]. The quality of this interface further depends on the state of the implants surface [5–7]. The implant surface has to be contaminant-free, while roughness is a desirable morphological feature as it plays a significant role in the tissue integration [5–7]. One of the possible methods for surface sterilization and enhancement of roughness is a laser treatment. Also, in the context of implant bio-integration one more aspect needs to be considered – the chemical reactions at the implant surface. Creation of different compounds on Ti-implant surface initiated by lasers, e.g. titanium-oxide(s) and titanium-nitride (TiN), in air/nitrogen atmosphere, can be additionally favorable [10]. Titanium-oxide(s) on the surface [4,10] can: (i) provide corrosion resistance of the implant sample, (ii) influence the implant surface adhesion properties, and (iii) lead to local hardening and improvement of the implant wear resistance. The presence of TiN on the implant surface is highly desirable, too [11–13]. TiN, among other things, (i) provides longer clotting time which makes it suitable for a blood contact implant, and (ii) shows high level of hardness. Generally, the present work deals with the laser surface modification of a Ti-implant in different gas atmospheres.

Interest in the studies of laser beam interaction with titanium was intensified in the last two decades. Different types of laser systems including excimer [6,7], Nd:YAG [10,14], Ti:Sapphire [15,16] and TEA CO_2 [17,18], have been employed for these purposes.

Interaction of titanium implant with a nanosecond TEA CO_2 laser beam in different gas atmospheres, with moderate laser fluences of ~30 J/cm^2 (laser intensity of 10^8 W/cm^2), was not sufficiently examined according to our knowledge. In the present paper our emphasis is on studying the effects of a nanosecond TEA CO_2 laser

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Table 1
Typical parameters of the TEA CO_2 laser used during irradiation of a titanium target.

Gas mixture content	$CO_2/N_2/He = 1/1/4.7$
Gas mixture pressure (atm)	1
Output pulse energy (mJ)	Up to 150
Energy density-fluence (J/cm^2)	Up to 30
FWHM[a] (ns)	~100 (initial spike)
Peak power (MW)	~0.5
Peak power density (MW/cm^2)	Up to 100
Mode structure[b]	Multimode output (typical)
Spectral emission[c] (μm)	10.5709 and 10.5909
Repetition rate (Hz)	Up to 2

[a] Full width at a half maximum. The TEA CO_2 laser pulse consists of an initial spike and a tail. The tail duration is about 2 μs. Approximately 35% of the total irradiated laser energy is consisted in the initial spike.
[b] Highly multimode output.
[c] The TEA CO_2 laser simultaneously operates at two wavelengths, i.e. 10.5709 and 10.5909 μm, P(18) and P(20) transitions.

emitting in the infrared region (~10.6 μm) on a titanium surface in air ambient, as well as nitrogen, oxygen and helium-rich atmosphere. Special attention was paid to morphological surface changes of titanium in these gases.

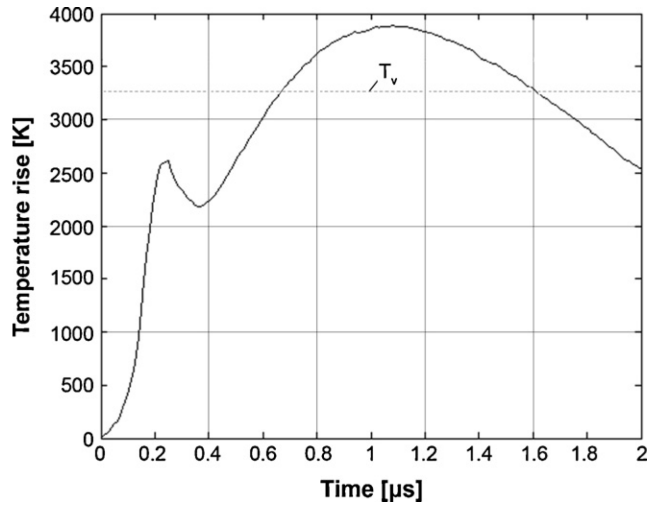

Fig. 1. Variation of the titanium implant surface temperature during TEA CO_2 laser irradiation.

2. Experimental

Surface modification experiments were conducted on the rectangular shaped samples of dimensions 25 mm × 15 mm × 1 mm. Titanium implant surface was prepared by a standard metallographic procedure. The samples were mechanically polished (first by using SiC grinding paper (360–1200 grit) and finally by using diamond paste (1–0.25 μm)), ultrasonically cleaned and dried in hot air. Prior to laser irradiation they were cleaned in ethanol.

Samples were irradiated by a laser beam focused using a KBr lens of 6 cm focal length, and directed perpendicular to the target surface. During irradiation process the laser was running in the multimode regime at a repetition rate of 2 Hz.

The irradiation was carried out in gas atmosphere of air, N_2, O_2 or He, at a pressure of 1013 mbar and standard relative humidity. Different gas surroundings were provided by a mini-nozzle situated in front of the sample surface. The nozzle was connected with flow meter and gas cylinder. Typical gas flow rate during the experiment was about 1 l/min.

The laser employed is a commercial TEA CO_2 laser system developed at the VINCA Institute [18]. The laser is miniature, compact system and its main characteristics concerning the experiment are given in Table 1. The optical pulse had a gain switched peak followed by a slowly decaying tail. Full width at a half maximum of the peak is about 100 ns, while the tail duration is ~2 μs. About 35% of the total irradiated laser energy is consisted in the initial spike.

Various analytical techniques were used for characterization of the titanium implant samples before and after laser irradiation. Elemental analysis was conducted by inductively coupled plasma (ICP), and the surface morphology was monitored by optical microscope (OM), scanning electron microscope (SEM) and atomic force microscope (AFM). The SEM was connected to an energy dispersive analyzer (EDX) for additional determination of the surface compositions. Profilometry was used for specifying the geometry of the ablated area.

3. Results and discussion

Elemental analysis of the titanium surface, performed by EDX/ICP before laser irradiation showed the following content: titanium ~93.4 wt.%, balanced to 100% by O (~4.3 wt.%), C (~wt.2.2%) and Al (~0.1 wt.%). Non-irradiated titanium surface had a typical silver-white metallic color and the surface roughness of the samples, obtained by profilometer, was less than 0.6 μm.

Surface modification of the target generally depends on the laser output parameters (pulse energy, energy density, intensity, wavelength, pulse duration, number of accumulated laser pulses, etc.), physico-chemical characteristics of the material, as well as irradiation conditions (working atmosphere – air, gas atmosphere, vacuum, etc.). The types of formed morphological features, determined among other by the surface temperature reached at the irradiated area, are different. These effects depend, beside other, on the so-called heat affected zone (HAZ) which represents the heat flow into the surface. For these experimental conditions it equals about four microns. In case of nanosecond TEA CO_2 laser interaction with titanium depending on the pulse intensity, a series of processes, such as heating, melting, vaporization of the molten materials, dissociation, ionization of the vaporized material, plasma creation, shock waves in the vapor and the solid, etc., can occur. These physical processes were studied in details on a number of metals, in various atmospheres, under the action of pulsed lasers, in [19]. Considering the laser intensity of 10^8 W/cm^2 used in our experiments, the plasma is formed in front of the target. Plasma affects the surface in several ways – by energy transfer, momentum transfer, and chemical reaction in the presence of active gas [20].

Temperature change on the target surface due to nanosecond laser irradiation can be estimated using the simple one-dimensional heat-conduction equation [21]. Calculated temperatures of the titanium surface, for our laser parameters, are presented in Fig. 1. Laser was mainly used in a multimode regime, and parameters of the laser pulse with tail are given in Table 1. The maximum laser intensity was 10^8 W/cm^2, and the target absorptivity 5.5%. Other Ti parameters, density of 4.52 g/cm^3, specific heat equal to 0.52 J/gK and heat diffusivity of 0.094 cm^2/s, are employed from Ref. [22]. It can be seen from the graph that the surface temperature surpasses the vaporization temperature of titanium. The reached temperature is sufficient to melt the metal surface and activate the gas above the molten surface, promoting chemical reactions between the material and surrounding gas.

Morphological changes of the titanium implant, depending on the number of accumulated laser pulses and gas atmosphere used, are shown in Figs. 2–6. The observed differences in the induced surface features will be discussed in the following: