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CURRENT TOPIC / АКТУЕЛНА ТЕМА

Laser surface modification of metallic implant materials

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SUMMARY

Metallic biomaterials are most commonly used as hard-tissue replacements because of their favorable mechanical features and excellent biocompatibility.

The objective of this paper is to present an overview of diverse surface modification techniques, with a special emphasis on the laser surface modification method, as well as diverse characterization techniques used for investigating the impact of the surface modification process on metallic implant materials' properties. Moreover, the effect of laser radiation on the surface its and mechanical characteristics, as well as on the structure of metallic bioimplants, is presented. The study of influence of high-intensity laser radiation on metallic materials' surface includes primarily investigations of the surface morphology modifications and specific surface structure formation since their presence enables enhanced osseointegration.

Keywords: metallic implant materials; laser radiation; surface modification; osseointegration

INTRODUCTION

Biometallics are metallic materials used in contact with cells, tissues or body fluids of the human body with the purpose of replacing or upgrading structural components of the human organism as a compensation for hard-tissue damage which may occur due to aging, illnesses, or accidents [1, 2].

Metallic implant biomaterials have been in use since the 19th century in a wide range of dental, orthopedic, cardiovascular, and other medical applications [1]. Stainless steels, cobalt-chromium alloys, and titanium-based materials are the main biocompatible metallic materials used in biomedical engineering [1–6]. Due to their excellent electrical and thermal conductivity, mechanical properties, and corrosion resistance, metallic biomaterials have been and will continue to be an essential part of medical devices in the future [2]. However, biometallics show some undesirable characteristics and because of that their further development is of prime importance [1, 6].

Biometallics must meet certain criteria in order to be used in biomedicine (see Figure 1) [1, 6].

High osseointegration ability is the essential requirement which all biometallics must fulfill [1]. Osseointegration is a process of the direct interface formation between an implant and a bone, without a negative effect on the surrounding soft tissues [5]. The inability of the implant surface to connect with the adjacent bone and surrounding tissues will cause the formation of fibrous tissue around the implant and, in turn, promote prosthesis release [7]. Therefore, it is necessary for an implant to have an appropriate surface morphology, i.e. surface chemistry, surface roughness, and sur-

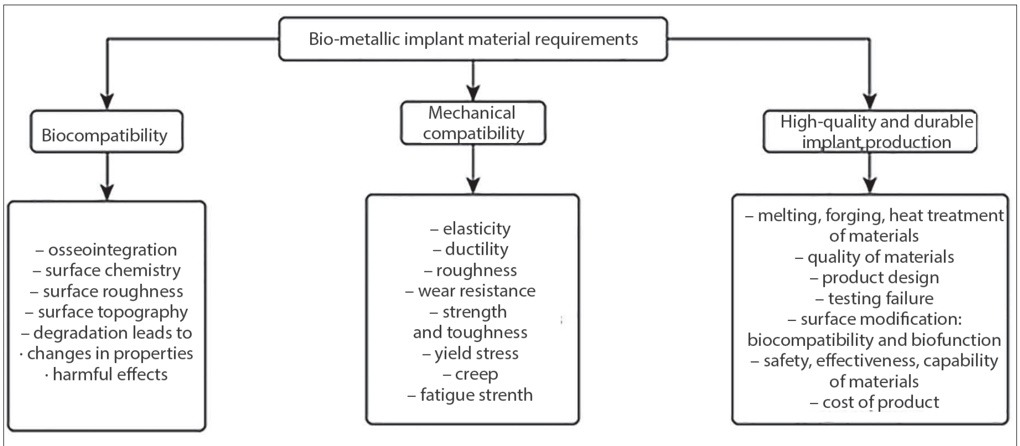

Figure 1. Implant material requirements for biomedical applications

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face topography, which will ensure its good integration. Accordingly, the implant surface modification is desirable in order to achieve improved biomechanical-biofunctional balance [8].

LASER SURFACE MODIFICATION

Surface modifications are used to improve implant biocompatibility and bioactivity, as well as to ensure proper osseointegration, with the objective of changing the surface physicochemical properties in order to improve bone healing and load transfer [7]. This can be achieved by altering the surface topography or by modifying surface chemistry.

Possibilities of changing/processing the surface of different biometallics using laser radiation are numerous and consequently various modern surface treatment techniques, such as ion implantation or coating, have lost their precedence in favor of laser processing [7, 8, 9]. Nowadays, lasers find widespread application in the medical device industry.

A laser represents a source of light radiation that emits a coherent photon beam, and as a source is stable in frequency, wavelength, and power [9]. In relation to other light sources, laser radiation is monochromatic, spatially oriented, intense, and coherent. All emitted photons of a laser beam, unlike photons in spontaneously emitted radiation, are completely identical, i.e. they have the same direction and phase.

The interaction of laser radiation and metallic targets depends on the characteristics of the laser radiation source, as well as on structural, optical and thermodynamic characteristics of the target, the focusing method, and the type and pressure of the surrounding atmosphere [10]. Laser radiation that falls on the surface is partially absorbed and partially reflected. Absorbed radiation causes heating, melting, and evaporation of the material.

A very important parameter describing the breakthrough of radiation into the material is the depth of absorption or optical breakthrough of light (Figure 2) [10]. By selecting radiation with low absorption depth, local changes in surface properties can be obtained without changing the (interior) volume of the material.

There are two mechanisms of removing surface particles using a laser: 1) laser-induced desorption (without any visible mesoscopic changes in the surface composition and structure) and 2) laser ablation (visible changes in the surface structure and composition) [11]. Laser-induced desorption and laser ablation are not completely separated, independent phenomena. Therefore, desorption and ablation should be observed as two phases in the process of laser interaction with the surface of the material [11].

Lasers provide directing a large amount of energy to a limited target area in order to achieve the desired material modification [7, 9, 10]. During the interaction of electromagnetic radiation with a solid target, the following changes can occur: radiation damage in the crystal lattice, structural changes leading to amorphization of the target and recrystallization in the collision zone, changes in the

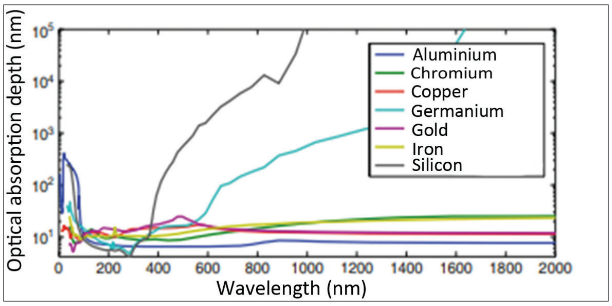

Figure 2. Optical absorption depths for diverse materials over a wide range of wavelengths [10]

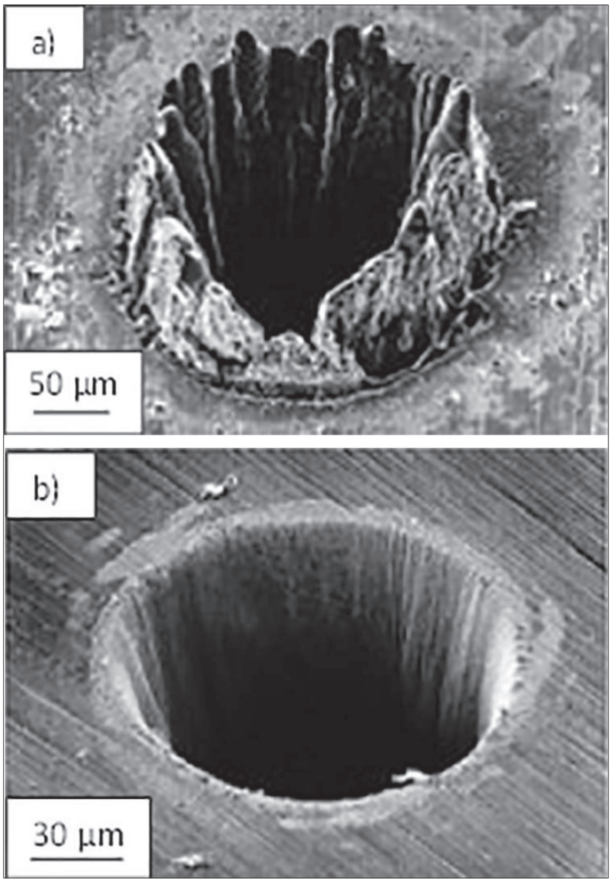

Figure 3. Craters obtained as a result of a) the femtosecond and b) the nanosecond laser radiation interaction with a steel surface [10]

chemical composition of the target, and changes in the target surface topography caused by erosion and redeposition.

The laser radiation-induced changes to the target surface depend on the characteristics of the laser beam, the number of accumulated impulses, the optical and thermophysical properties of the material, and the irradiation conditions (Figure 3) [7, 10].

If plasma is generated during the interaction of laser radiation with the material, it can significantly affect the intensity by which the radiation is acting on the surface and thus affect the formation of the crater [12]. The interaction of incident laser radiation and plasma can be expected during the use of a nanosecond and picosecond radiation, while in the case of ablation with femtosecond radiation, this interaction is absent.

LASER MODIFICATIONS OF IMPLANT MATERIALS

The surface morphological changes due to the action/interaction of the laser with the surface of the implant material can be examined using various techniques, such as light optical microscopy, scanning electron microscopy, energy dispersive spectroscopy, and profilometry [7, 13]. The first information on the surface morphological changes is obtained by light optical microscopy and scanning electron microscopy, while energy dispersive spectroscopy allows an estimate of the surface elemental composition. Topographic changes and specific surface geometry of the areas modified by the laser irradiation are analyzed by contact and non-contact profilometry.

Torres et al. [8] showed that in the case of the Ti-6Al-4V alloy, laser treatment in combination with different chemical and thermo-chemical treatments (etching and chemical oxidation) can enhance the surface bioactivity due to the formation of a stable titanium oxide layer. The laser modified surfaces manifested a rough surface covered with submicro- and nanopores.

If the energy density is close to the threshold of damage, formation of structures in the form of periodically repeated parallel waves can be expected while the surface of the target metallic material is being irradiated by the laser [14]. These structures are designated by the term laser-induced periodic surface structures (LIPSS). An important requirement for the occurrence of LIPSS is the surface roughness that allows for the intersection of the incident beam so that the polarized light, normal to the surface, can initiate electronic oscillations.

It is obvious from Figure 4 that the accumulation of a large number of impulses on the target, at a constant energy density and with different lasers, leads to an increase in the ablation depth and surface traces formation [13]. Zhang et al. [7] noticed that the laser beam radiation performance in a single-pulse and multiple-pulse mode results in different depths of damage. Ablation results in the formation of a prominent crater and the removal of the dissolved material from the surface.

Comparing the specific surface features obtained during the irradiation of a titanium implant in gaseous (air) and liquid (water) mediums, Trtica et al. [14] concluded that the liquid medium is a better choice for laser surface treatment since it results in better surface roughness (Figure 5). Also, the appearance of LIPSS is observed on the surface in both environments. In water environment, LIPSS are recorded after low-impulse interaction, while in the air atmosphere they occur after high-impulse interaction. It was found that during irradiation in the air, oxygen was absent from the central part of the laser beam, while its concentration was relatively high in the presence of water.

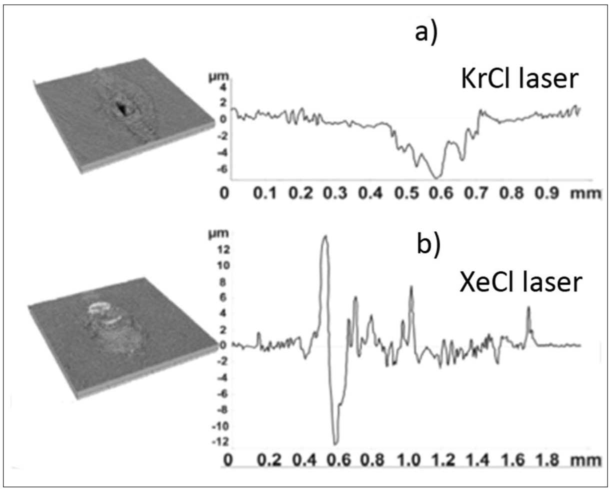

Figure 4. Profilometric analysis of the Ti-6Al-4V alloy surface after modification using a) KrCl and b) XeCl laser [13]

The water also shows a high oxidation capacity that stimulates bioactivity of the surface.

Trtica et al. [15] observed that irradiation treatment of titanium at high intensities contributes to the formation of large craters after a few pulses, and as the number of pulses increases, the creation of the surface craters with periodic structure can be expected. These properties enhance the titanium implants' biointegration potential. Also, wavelength increase results in more visible surface damage.

Laser modification improves the surface roughness [14, 15, 16]. In the air and oxygen atmosphere, the resulting surface structures correspond to the smooth, periodic dome structures. In the presence of increased oxygen concentration, an oxide surface layer is formed. In the nitrogen atmosphere, the obtained surface structure is non-compact and porous. The surface structure formed in the helium atmosphere is completely different and the presence of micropores can be noticed.

Hermann et al. [16] noticed that the presence of plasma protects the titanium surface from radiation and that further heating of the material can be achieved through the

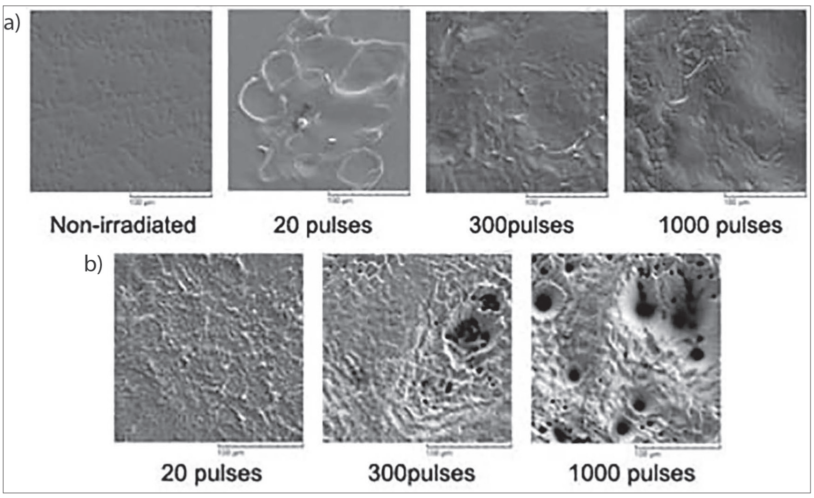

Figure 5. Scanning electron microscopy analysis of the Ti implant (target) surface after irradiation with picosecond laser pulses in a) air and b) water atmosphere [14]

plasma itself. A better transfer of energy to the material is achieved in the helium atmosphere.

LASER EFFECT ON THE IMPLANT TRIBO-MECHANICAL PROPERTIES

Wear occurs during relative movement of the joint parts that are in contact with each other, and results in the component damage [5]. The type and severity of the wear damage depend on many interaction factors and can be accompanied with processes such as corrosion, which in turn leads to the increased material loss and in extreme cases fast metallic implant failures.

Laser surface modifications can enhance wear resistance and friction properties of the implant [17]. Chen et al. [17] demonstrated that surfaces treated with high laser power showed higher hardness and wear resistance than the untreated and surfaces treated by low laser power.

One of the laser modification methods, used to improve mechanical properties, corrosion resistance, biocompatibility and wear resistance, is laser cladding [18]. Laser cladding enables the formation of the protective coating on the alloy substrate surface. Also, laser alloying, laser heat-treatment, and laser overlaying are methods which can be used in order to enhance the implant material hardness, wear, and corrosion resistance [19].

Low hardness values and poor tribological characteristics of metallic implant materials can be improved by laser powder deposition [18]. Comparing the Ti-6Al-4V substrate characteristics with the characteristics of the Ti-Al intermetallic coating formed on the Ti-6Al-4V alloy surface (Figure 6), Liu et al. [20] noticed that intermetallic coating displays lower friction coefficients due to the higher hardness values since the biometallics hardness and wear resistance are greatly influenced by each other [17–20].

The alloy microstructural characteristics, such as phase composition and grain size, greatly affect and determine alloy mechanical properties [5, 21]. There are numerous laser irradiation methods which can contribute to the achievement of excellent implant mechanical properties [21]. One of those methods is laser surface remelting. Using this method, grain refinement can be obtained in the remelting zone. Diagrams presented in Figure 7 show a great improvement in mechanical properties achieved by laser treatment [21]. Laser surface remelting increases the elastic modulus and hence metallic material stiffness and hardness, throughout the material microstructural transformations. From Figure 7 one can observe that the hardness value is the highest in the remelting zone, and the lowest in the metal substrate zone. This also applies to the elastic modulus.

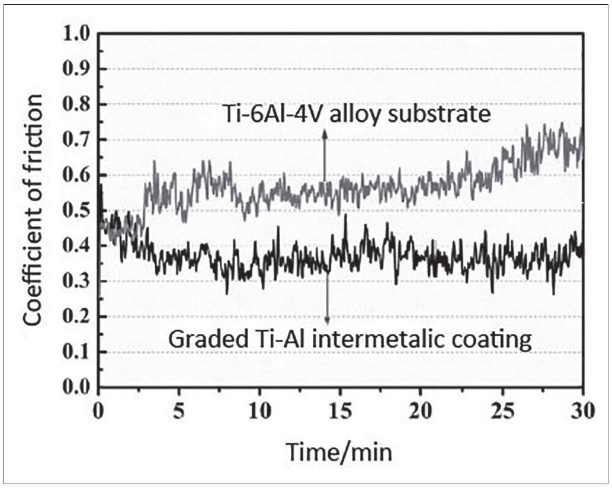

Figure 6. Friction coefficients variation for the Ti-6Al-4V substrate and Ti-Al intermetallic coating [20]

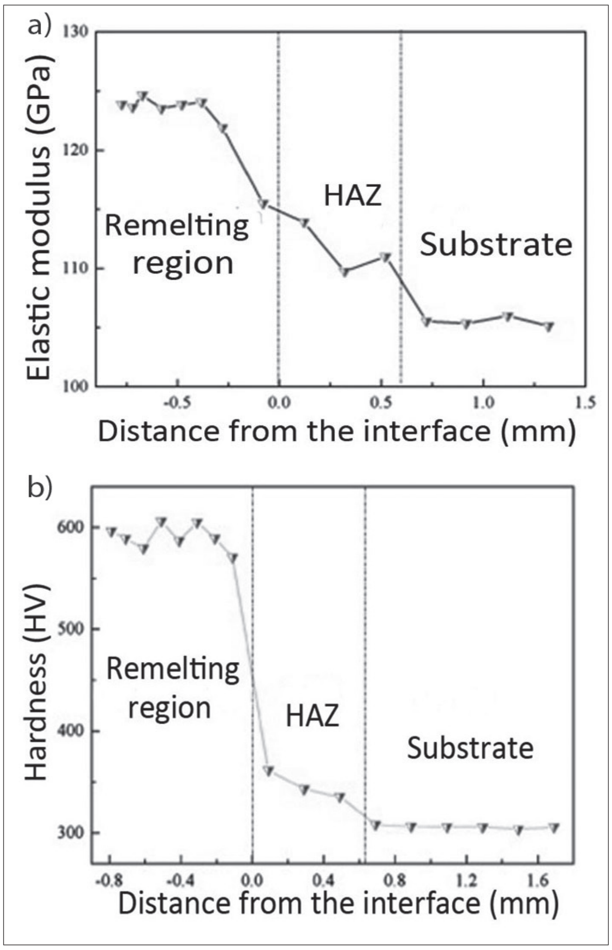

Figure 7. Elastic modulus a) and hardness b) of the Ti-Zr alloy in different laser-treated regions [21]

CONCLUSION

When developing new materials for biomedical applications, most attention is devoted to implant material biocompatibility, non-toxicity, and osseointegration. Desirable characteristics of bioimplants can be achieved by surface modifications. Laser surface modification is one of the methods by which the enhancement of mechanical, physical, and tribological characteristics can be obtained. Excellent surface roughness, high hardness value, outstanding biocompatibility, and implant surface bioactivity, non-toxicity, excellent corrosion and wear resistance, low friction coefficients and porosity can be achieved. The interaction of laser pulses with the metallic implant material surface causes changes in the surface morphology, optical characteristics, chemical composition, etc., according to the selected parameters of the laser beam. Surface periodic structures can be formed by laser modification, and the appearance of these structures can influence the improvement of the implant surface characteristics and implant osseointegration.

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Conflict of interest: None declared

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Ласерска површинска модификација металних имплантантних материјала

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САЖЕТАК

Метални биоматеријали се најчешће користе за израду имплантаната чврстих структурних делова људског тела због својих добрих механичких карактеристика и одличне биокомпатибилности.

Циљ рада је да се прегледно представе различите технике површинске модификације имплантантних материјала са посебним освртом на методу ласерске модификације површине, као и многобројне карактеризационе методе за испитивање утицаја процеса површинске модификације на својства металних имплантантних материјала. Осим тога, представљен је и разматран утицај ласерског зрачења на површинске и механичке карактеристике, као и на структуру металних биоимплантаната. Испитивање утицаја ласерског зрачења високог интензитета на површину металних материјала првенствено обухвата испитивање морфолошких површинских промена и формирања специфичних површинских структура, које доприносе побољшању осеоинтеграције металних имплантаната.

Кључне речи: метални имплантантни материјали; ласерско зрачење; површинска модификација; осеоинтеграција