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Preparation of calcium phosphate coatings on titanium by pulsed Nd:YAG laser processing

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The biocompatibility, osteointegration of the titanium implants, which are mainly used in oral surgery depends essentially on both the morphology and the chemical composition of the interface between the bio-tissue and the implant. In addition to the known laser-based methods of increasing the roughness, changing the morphology of the surface and enlarging the effective tissue-implant contact area, pulsed Nd-YAG laser processing of the surface in the presence of hydroxyapatite (HA) and tricalcium phosphate (TCP) was performed. More versatile bioactive coating may be created in this way in comparison with the known plasma spray method. Optical and electron microscope investigations as well as EDX revealed that a specific surface microstructure, micro-heterogeneous titanium-calcium phosphate coatings can be fabricated by the developed method which may further influence the osteointegration of Ti implants due to the changes of surface morphology, mechanical and chemical stability, bio-activity.

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1. Introduction

Titanium (Ti) is one of the best known materials for implants and is widely used for long-term implants in surgery and in dentistry because of its high mechanical performance, good resistance to corrosion and biocompatibility [1]. These characteristics are largely determined by the composition (presence of impurities, phase structure [2]) and by the macro- and micromorphology of the surface [3]. The surface roughness seems to promote the growth of the bone and fortify the interconnection between the implant and the native tissue [1, 2, 4]. The integration with bone tissue can be improved and accelerated by the presence of bioactive materials at the surface, especially by different calcium phosphate coatings [1]. Bioactive and osteoconductive HA ($Ca_{10}(PO_4)_6(OH)_2$), TCP ($Ca_3(PO_4)_2$), and other calcium phosphate materials promotes direct attachment to bone tissue [5, 6] and have been extensively applied to improve fixation between metal implants and bone tissue [7]. But sometimes it is mentioned that the efficiency and the mechanical stability of the cover is problematic, the solubility is not suitable [1]. These and other parameters may be improved by biomimetic deposition of HA or calcium phosphate coatings in simulated body fluids [8], by pulsed laser deposition of HA [9] or by the formation of gradient Al_2O_3 – HA structures plasma sprayed onto the Ti surface [10].

But the problem of operated roughness of the surface, its stability, characteristics of calcium phosphate coatings with a certain chemical composition and structure needs further investigations. The influence of the surface topology and composition on morphogenesis depends on the cell type as well as on the cell adhesion, interaction with other cells and on the bone type [1, 11]. Therefore, various and efficient technologies of surface modification must be used to fulfill the requirements of different applications.

The well polished surface of the titanium (usually the hard β-phase or an α+β mixture, which can be produced by heat treatment or by Al, V- doping) may be obtained as a consequence of mechanical, chemical and plasma treatments. Such treatments can wipe off surface contaminations. Certain type of surface morphology with optimally ~1-2 μm roughness may result. Combined cycle of surface polishing and further processing by nanosecond excimer laser pulses was performed in [12]. High intensity IR laser pulses were used by some authors [13, 14] to modify the surface of titanium dental implants. Titanium oxide covers the surface in a short time and such oxide layer will appear following all types of surface roughening and maintaining in a normal atmosphere. The presence of thin (~20 nm) or even thicker oxide layer is usually not a matter of discussion when the surface pattern is examined at 1-100 μm dimensions but some works are focused just on the parameters of titanium oxide layer at the surface [15, 16], the role of which in osteointegration is not yet known in details. Laser fabrication of the surface of Ti seems to be the most suitable and clean (with a wide range of temperature, time, ambient variations during the treatment) and can be combined with mechanical or chemical modifications. New route of HA attachment to the Ti surface by pulsed laser treatment was proposed in our earlier work [17] the efficiency of which was

supported later by the results in [18]. We continued these work towards the investigation of structure and composition of HA and TCP layers on Ti obtained by pulsed Nd:YAG laser processing.

2. Materials and methods

A series of flat samples were made by cutting from a commercially available pure titanium (BS2TA2, Titanium International) or, for comparison, from a special non-annealed Ti plates. 2 mm thick samples with 10×10 mm^2 surfaces were mechanically sandpapered and cleaned ultrasonically in ethanol and distilled water. These samples were used for laser processing with or without two types of calcium phosphates (CP) simply mechanically attached (pressed) to the surface or mixed with adhesive and spread on substrates. The first type of initial samples was covered by a layer of hydroxyapatite granules with 40 μm average size, which in turn consist of smaller, 1-2 μm large grains (KERHAP, product of IPM, Kijev, Ukraine). The second type was covered by a layer of TCP grains with 10 μm average size (REANAL, Hungary). If the layer of CP grains was formed by spreading a CP-containing adhesive, the sample was preliminary dried and annealed to burn out the adhesive.

Laser processing of the surface was carried out in a chamber at normal atmosphere conditions using the 1.06 μm wavelength output of an Nd:YAG laser (1 in Fig. 1) having regulated duration τ and energy of the pulse in 3-5 ms and 2-8 J range respectively. The focused laser pulses interact with the surface in a ~2 mm^2 area. If a special cylindrical lens is used, a more uniform scanning of larger area is possible. The sample was placed on a positioning stage (4 in Fig. 1), so it was possible to scan the surface with laser pulses with or without overlapping each other and to produce large areas covered continuously or by islands of CP (see Fig. 2).

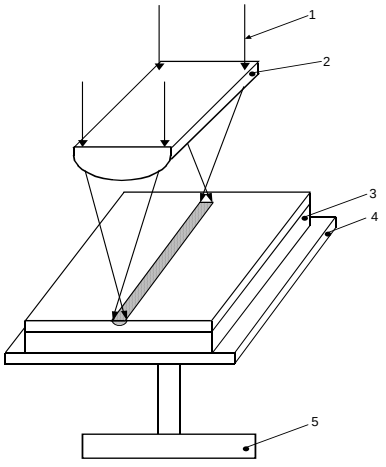


Fig. 1. Experimental setup of the laser processing. 1- laser beam, 2- round or cilindrical lense, 3- Ti sample without or with CP grains on its surface, 4- positioning stage, 5- scanning system.

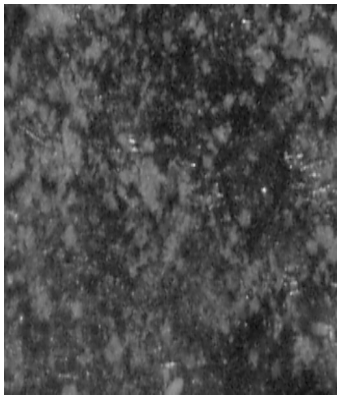


Fig. 2. The Ti surface covered with HA after pulsed laser processing (60x magnification, optical microscope).

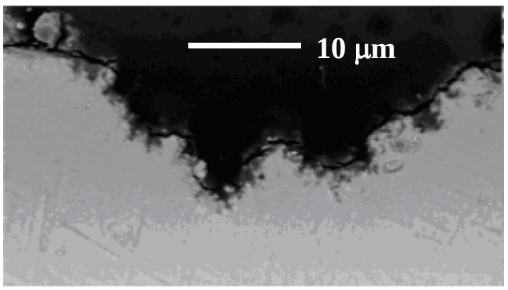
The surface morphology was investigated by optical microscope (Carl Zeiss, AXIOTEC) as well as by scanning electron microscope (Hitachi S-4300). Cross-sections of the sample along the path of laser pulses were also made. The average composition of the coating was measured by energy dispersive X-ray analysis (EDX) at the same SEM from the top or along the cross-section of the sample.

3. Results and discussion

The surface of the initial Ti substratum usually consists of 0.5-1 μm deep sporadic scratches and holes due to the sandpaper treatment. The Ti surface processed by Nd-YAG laser shuts in the above mentioned regimes may become even more rough at different length scales from micro- to nanometers. Usually we obtain arranged, up to the few μm deep craters with rims, if the delivered energy is above 3.2 J ($P=4{,}8\times10^4$ W/cm^2) in one pulse (see Fig. 3, a). The roughening occurs via deformation of the pulse-heated surface and, possibly, its' additional oxidation enhanced according to the local temperature distribution, as it was supposed also in [14, 15]. The temperature of the surface at the moment of irradiation by such a pulse can increase above 2000 K, i.e. the surface of Ti can be melted ($T_m \cong 1650\ ^\circ C$). This was supported by the estimations according to the model of two-layer system [19] as well as by the presence of phase-changed volume at the surface of the appropriate sample (the „soft" α-phase Ti transforms to the hard β- or α+β phase due to rapid heating above 1153 K and cooling) The micro hardness of the treated surface essentially increases in this case from 2.5 to 8.8 GPa. Therefore we can calculate with a surface melting and roughening due to the pulsed YAG-laser treatment of the proper Ti sample.

The next step of our experiments was the pulsed laser processing of Ti surface, which was preliminary covered by a layer of granular hydroxyapatite or tricalcium phosphate. Since the optical transmission of such granular layers at the YAG-laser wavelength was near or higher than 50 %, the Ti is heated up and the reaction of the calcium phosphate with Ti at the interface occurs. It seems

from the photos (Fig. 3b) that HA grains are little "melted in" into the surface due to the laser pulse action, decompose and transforms to other structures resulting in a gradient reaction layer between the HA and Ti, which fill in the surface voids. This layer can not be easily removed from the surface, i.e. the mechanical stability is better as in the case of pure plasma sprayed HA coating. The decomposition is not so pronounced in the case of TCP, although the structural transformation is visible (the tricalcium and tertacalcium phosphates are stable at the Ti melting point).



a)

b

Fig. 3. a) SEM picture of the cross-section of a spot on Ti surface shot by a laser pulse ($P>5.10^4$ W/cm^2). b) Optical micrograph of the cross – section of Ti sample laser processed in the presence of HA grains ont he surface.

So, the morphological elements of the laser processed calcium phosphate+Ti surface consist mostly of craters and bumps with different compositions in 1–60 μm range. They cover the surface quite homogenously as it is seen in Fig. 2, but the space is not filled by HA or TCP only: other phases are visible between the grains, as it is clear from the cross-section SEM data (see Fig. 4 and Table 1). For this reason the EDX analysis from the top gives the average composition of the cover layer which differs from the known calcium phosphate composition.

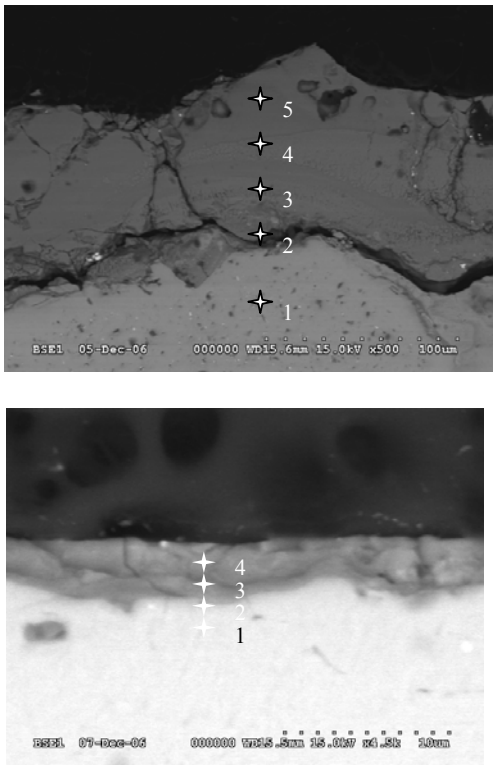


Fig. 4. SEM pictures of the cross-sections of laser processed HA-Ti (a) and TCP-Ti (b) surfaces.

The surface voids, which are created during the mechanical treatment and laser shoot, are filled up and a hard cover layer with islands are formed. A mixture of oxides and calcium phosphates with a locally changing depth profile are formed as a result of pulsed laser treatment of the HA-Ti system. In the TCP-Ti system the cover layer seems to be more homogeneous. It may be caused by the smaller thickness of the initial TCP layer at the surface (smaller diameter of the granules) and by the higher stability of TCP. The rapid heating and cooling of the comparatively thick (usually more than 20 μm) multicomponent layer causes local stresses which can lead to cracks.

Table 1. Composition C (at. %) of the coatings in the points in Fig. 4.

Element	HA coating					TCP coating			
	$C_{p.1}$	$C_{p.2}$	$C_{p.3}$	$C_{p.4}$	$C_{p.5}$	$C_{p.1}$	$C_{p.2}$	$C_{p.3}$	$C_{p.4}$
Ti	98.85	24.38	8.33	5.59	4.97	98.69	20.65	4.18	2.59
Ca	0.57	23.64	25.21	25.85	28.39	0.58	8.88	23.48	23.58
P	0.55	2.70	10.15	10.64	11.02	0.70	5.51	12.98	13.12
O	0.03	49.28	56.31	57.92	55.62	0.03	64.96	59.36	60.71

A more detailed analysis of the process was done to determine the composition of the resulting covers. It was expected that CP grains can be introduced into the melted Ti without total melting and decomposition, if the experimental conditions (temperature of the Ti surface, heat conductivity and transparency of the CP with a given thickness) are optimized. The local EDX analysis of the surface as well as of the cross-sections showed that certain gradient interface layer is created. It can start from the pure HA at the top (if the grains are not completely decomposed, like in Fig. 3b) or from the decomposed phases (like in Fig. 4) and changes towards the pure Ti in a way, presented in Fig. 3 b, Fig. 4 and Table 1 for a given intensity of laser pulses. EDX data reveals the gradient of Ti, Ca, P and O in the cover layer, which may not contain pure HA or TCP grains at the top if the thickness to pulse energy ratio is small, i.e. the whole initially granular layer undergo changes due to the laser heating, interaction with molten Ti, and decomposition.

Lowering the laser pulse intensity to the optimum results thinner transition layer and presence of original CP phase at the surface. Furthermore it can be seen in Table 1. That in the completely molten layer the Ca: P: Ti: O ratio changes in depth in a rather similar way both for HA and TCP. The Ca/P ratio is more than 2 at the top in the case of HA on Ti sample, and little lower in the case of TCP-Ti. The deficit of P may be caused by the high thermal diffusion coefficients of P and Ca in titanium at elevated temperatures (10^{-8} cm^2s^{-1} [20]) as well as by the evaporation of P_2O_5 at the interface, where a mixed layer of CaO or $Ca_4Ti_3O_{10}$ dominate. The presence of some Ti signal at the top may be caused just by the roughness of the surface and a rather deep volume of analysis. The real structure of these layers, the possible crystalline or amorphous phases needs further analysis.

The mechanism of formation of the above reaction layers can be the following: at the irradiation of the original structure (Fig. 5a) since the melting temperature of Ti is possibly below the surface temperature given by the energy density of the laser pulse, first a thin melted Ti spot is formed at the interface (Fig. 5b). The diffusion and/or convection in this liquid phase can be fast enough to produce the observed structure during such short pulse duration as 10^{-3} s and even to form a continuous mixture layer (Fig. 5c.) with decreased P content. Phase changes and degradation of HA or TCP having as result the rise in CaO content were observed also at high plasma power level during the plasma sprayed HA coating production [20].

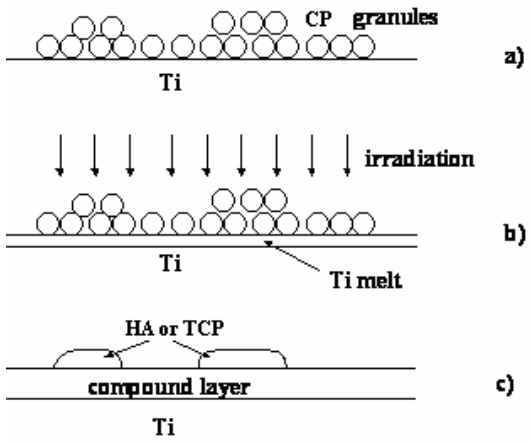


Fig. 5. A model of surface layer formation at the laser processed CP-Ti interface.

Besides better mechanical properties, adhesion and decreased solubility in body fluids Ca and P enriched Ti or Ti oxide layer are interesting because of the better adhesion of the coating layers and known influence on the regulation of bone cell interaction with titanium [21, 22]. Therefore the resulting complex multilayer may be considered as a versatile bioactive coating with parameters, which can be controlled by the composition of the initial interacting components and by the characteristics of the pulsed laser processing as well.

4. Conclusions

Micro- and macro-scale Ng-YAG laser processing of the Ti surface, including the new method of formation of heterogeneous, at the micrometer scale, interface layer containing Ca-P compound was realized. The enhanced reaction of Ti with HA and TCP creates phases with high mechanical and, possibly, increased chemical stability. The biocompatibility of such implant material also seems to be good, since in [20] the presence of Ti in a cover layer is evident, as well as in titanium oxide layers on all implants. Direct investigations of such structures *in vitro* are planned. The new method is suitable for incorporation of a wide range of other ceramic particles into Ti surface.

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