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MATERIALS AND TECHNOLOGIES USED IN PRESENT DENTAL IMPLANTS MANUFACTURING

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Abstract: *Starting from 2008 the authors collaborated in several research projects, having the full support of the Romanian manufacturer of dental implants, Tehnomed Impex Co S.A. The aim of the research projects was to improve dental implants in order to better osseointegration. Studied materials used for base structure of the implants were both materials for medical purposes acquired from industrial manufacturers and new designed materials for human implants. Materials used for superficial layers of dental implants were studied in vivo, respecting ethical issues, but the research has to be continued. Manufacturing technologies for implants were classic metal cutting and sandblasting, while the technology used for superficial layers was Pulsed Laser Deposition. The paper presents a brief review of these materials and technologies, also presenting research data and results in some cases.*

Key words: *Dental implants, titanium, zirconium, hydroxyapatite, βTCP, sandblasting, PLD.*

1. INTRODUCTION

Tissue engineering occurred as a promising solution to reconstruct lost or damaged tissues and organs, thus preventing complications of classic transplants [1].

In this research the lost or damaged tissue is tried to be repaired or replaced using tissue substitutes which are functional during tissue regeneration and eventually they are integrated into host tissue.

Both implant success and new tissue (re)construction depend on the selected material(s).

Biologic molecules and cells together with own properties of the selected biomaterial(s) influence biocompatibility and longevity of an implant.

In the following, will be presented information obtained by authors' own experience and research, related to conditions which lead to better osseointegration of dental implants.

2. MATERIALS FOR DENTAL IMPLANTS

From the beginning it must be underlined that in research were used two types of implants: real human dental implants, manufactured by Romanian manufacturer Tehnomed Impex Co S.A. using its own Romanian patent [2] and special disc implants used for in vivo research.

Present research related to dental implants materials all over the world studies the possibility to use new base structure materials and new superficial layers.

2.1. Materials for the implant's base structure

Even if there are many known metal alloys, very few of them may be selected as base structure materials for implants. Because of metallic implant corrosion due to the human body fluids ions of metal are released influencing vital processes. Corrosion resistance is not sufficient to avoid human body reactions to metal toxicity or allergy to specific elements. As an effect, the implant can be rejected.

Titanium is considered to be totally inert to the body fluids. For this reason it is considered to be the most biocompatible material.

Titanium comes in a very wide range of grades [3], out of which only the first four grades mean unalloyed titanium (purity of approx. 99%). Tensile strength of these grades rises from 240 MPa to 550 MPa (Table 1). This means the more impurities contains the pure titanium, the higher strength it has (see Table 1).

Human body anatomy limits the dimensions of the implant. This imposes higher strength, which lead to the practical conclusion that titanium grade 4 will be normally used as base structure material.

Table 1

Impure elements of pure titanium (ASTM F67-06)

Grade	Elements%					Rm
	Fe	O	H	C	N	MPa
Ti-grd. I	0.2	0.18	0.015	0.08	0.03	240
Ti-grd. II	0.3	0.25	0.015	0.08	0.03	345
Ti-grd. III	0.3	0.35	0.015	0.08	0.05	450
Ti-grd. IV	0.30	0.40	0.015	0.08	0.05	550

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An even higher strength has titanium grade 5, which is the reference titanium alloy, Ti6Al4V. Its typical tensile strength is 1 000 MPa.

Because Ti6Al4V is not pure titanium and because of its high strength, it is used in many cases for implants which have small dimensions and do not have contact with human body fluids (contact only with bone). This means dental implants could be made of Ti6Al4V in specific designed cases.

Having so many advantages, titanium and its alloys have also some important disadvantages:

- being a metal, it can make a pile inside the body, leading to the retraction of bone,
- its grey colour is unnatural into the mouth.

These disadvantages lead to the use of zirconia (ZrO_2) as base structure material for implants [4].

It has eliminated the disadvantages of titanium, but it has its own disadvantage, meaning its hardness. The dental implant made of zirconia can be manufactured by cutting only using diamond tools in case of Romanian dental implants manufacturing.

Because zirconium is material similar to titanium, it appeared the idea of making an alloy of these two metals.

In one research project a new alloy was elaborated using these two elements: titanium and zirconium. Because it was not yet patented, we will not give its composition, but will present research of its tensile strength.

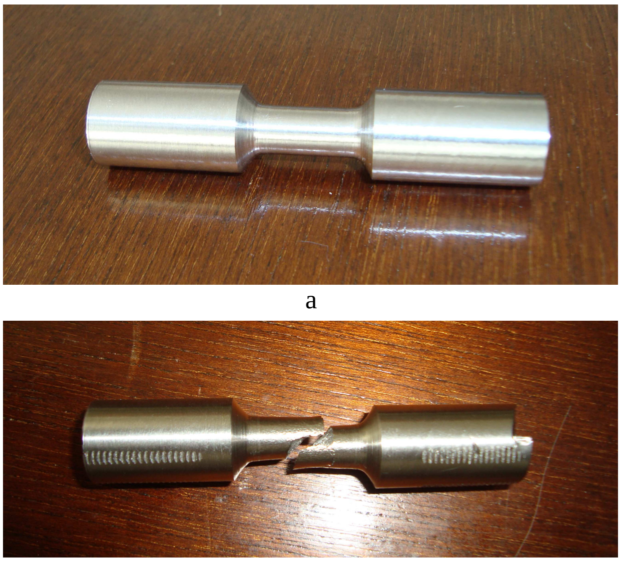
Research was done in University “Politehnica” of Bucharest, laboratory of Strength of Materials Dept. It was a tensile test, using a sample of the new material (Fig. 1).

The tensile test was done on INSTRON 8801 tensile testing machine having an INSTRON 3520 control equipment.

The test revealed taht the new material had a very high tensile strength, as seen in Table 2 and Fig. 2.

2.2. Materials for implant surface layer

Up today it is well known that titanium, being in contact to air or water, rapidly oxidizes and a thin layer of



a

b

Fig. 1. Sample of the new material: *a* – before tensile test; *b* – after tensile test.

Table 2

Tensile test results for the new material

Modulus (Automatic Young's) (MPa)	Tensile stress at Tensile Strength (MPa)	Tensile strain at Tensile Strength (%)
75303.48390	830.97295	24.51329

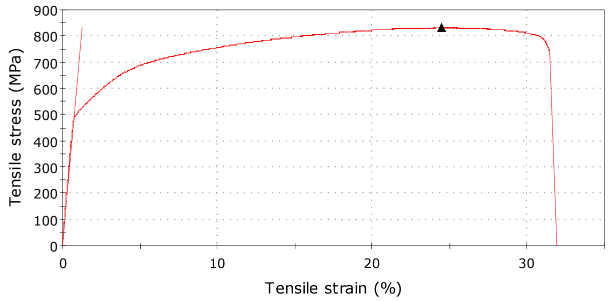


Fig. 2. Tensile test characteristic curve.

TiO_2 is formed. This gives to titanium implants a better corrosion resistance and a good osseointegration, in which the bone adheres to the implant without inflammation. This means that TiO_2 is a good surface layer for osseointegration.

Modern researches study new materials for surface layers, such as calcium phosphates, which are similar to the mineral substances in the bones and have a good response of the organisms being used in implants applications. In researches we used hydroxyapatite and βTCP (β-Tri-Calcium-Phosphate).

Hydroxyapatite (HA), Ca10(PO4)6(OH)2, is used as a model for inorganic compounds of the bones and teeth. It has the highest stability and the less solubility of all calcium phosphates.

HA with calcium deficiency, having the formula Ca10-*x*(PO4)6-*x*(HPO4)*x*(OH)2-*x*, $0 \le x \le 1$ and carbonated HA’s have great importance in biological systems, being major inorganic compounds of the bones and teeth. HA’s with calcium deficiency have the same ratio Ca/P as bones do (approx. 1.5), being more suitable to biological applications than stoechiometric HA [6, 7]. Chemical-biological processes as catalysis, ionic change and degradation in physiological solutions are strongly dependant on Ca/P ratio [7].

In order to improve mechanical properties and biological behaviour, hydroxyapatite may be doped with zirconia (ZrO2). Nanopowders used in these studies were produced by Latvian manufacturer, Plasma And Ceramics Technologies Ltd., in collaboration with Institute of Inorganic Chemistry of the University of Riga.

Calcium phosphates have also different forms, such as tri-calcium phosphate (TCP, having α and β crystallographic forms), di-calcium phosphate (DCP) etc. In 1920 Albee discovers that tri-calcium phosphate stimulates bone formation [8].

Researches were made *in vivo*, on rabbits, respecting ethical issues, using surface layers of HA and βTCP on disc and threaded prototype implants (Figs. 3 and 4). In case of disc prototype implants, disc implants having HA and βTCP submicronic surface layers [5] were used and in case of threaded prototype implants we used threaded implants having surfaced HA, βTCP and bioglass submi-

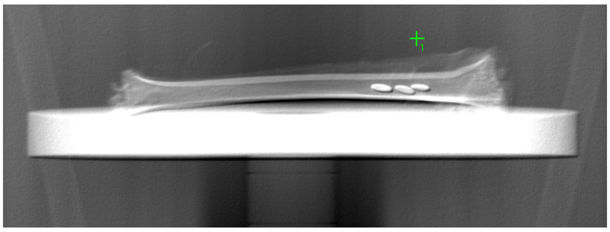


Fig. 3. Radiography of rabbit leg with disc prototype implants.

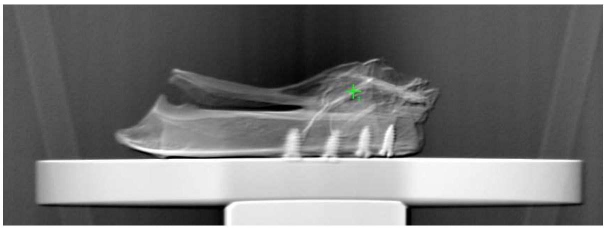


Fig. 4. Radiography of rabbit leg with threaded prototype implants.

cronic surface layers. Obvioulsy, reference implants having no surface layer, better said having only own TiO_2 surface layer, were also used.

Research results were inconclusive, meaning the number of experiments was too small. Still, as an intermediate observation, the surface layers of HA and βTCP were as good as TiO_2 own surface layer of the implants, from osseointegration point of view. This could mean, without being final, the naked titanium implants are as good as the implants having HA, βTCP and bioglass submicronic surface layers.

3. TECHNOLOGIES FOR DENTAL IMPLANTS

As previous told, dental implants are manufactured by classic cutting technologies. The news appears in details, meaning the surface of the implant.

Ideal surface of titanium implant has to present following characteristics:

- absence of impurities (foreign bodies),
- high chemical and mechanical stability,
- adequate morphology to a good cell adhesion and bone growth,
- adequate surface roughness for a good bone-implant interaction on long term.

The last two parameters are essential to body response. They can assure a rise of bio-compatibility up to 10 times.

3.1. Sandblasting

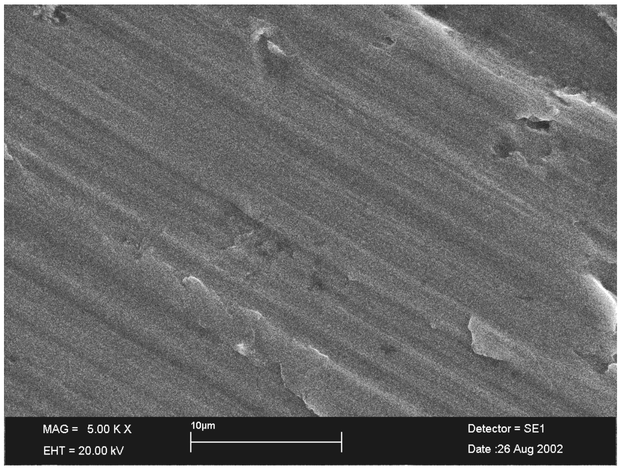
Many years ago, maybe more than 10 years, some Romanian researchers [2] designed a dental implant in two steps [2, 9], see paragraph 4. One of the problems to be solved is micro geometry of dental implant surface.

The average dimension of the bone cell is 0.02 mm to 0.03 mm. This means the surface micro geometry of the implant should have alveoli of same dimension in which bone cells will grow and live after.

The real manufacturing technology, which obtains these alveoli is sandblasting. This technology means impact between particles of sand (or particles of hard material, i.e. Al_2O_3) and base material of a workpiece, generally, a dental implant (human implant), especially.

Because the average alveoli dimension is 7–10% of the particle diameter, this means the used sandblasting particles will have 0.25 mm diameter.

There are also other technologies for obtaining surface roughness, but in case of dental implants sandblasting is the best from osseointegration point of view (Fig. 5).



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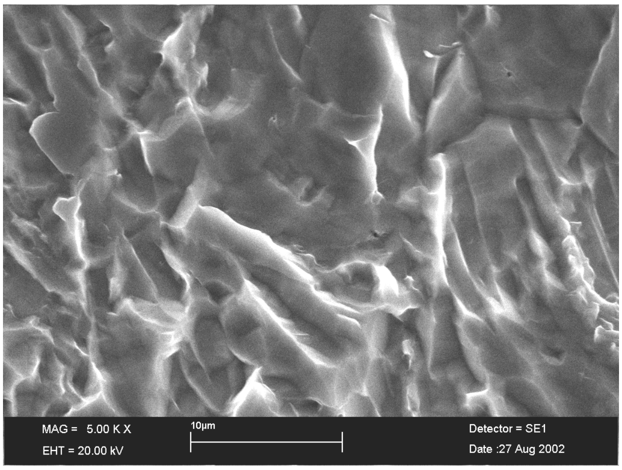

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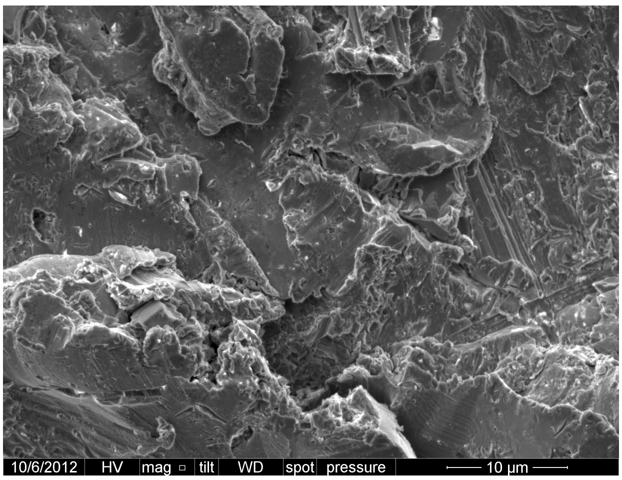

c

Fig. 5. Different technologies for obtaining micro geometry surface of the implants: *a* – typical mechanical polishing sample; *b* – typical corroded sample; *c* – typical sandblasted sample.

Obviously, as seen in Fig. 5, there are different technologies to obtain needed micro geometry of dental implant, but the real criterion to select these technologies is the cost. Sandblasting is one of the cheapest technologies of all technologies used in dental implants manufacturing. This is, obviously, the criterion used in real life by dental implants manufacturers to select used technologies.

The only disadvantage of sandblasting is that sand particles can be fixed into the dental implant surface during sandblasting, remaining onto the implant. This will surely cause the rejection of the implant by the human body. In order to avoid this disadvantage, all sandblasted dental implants should be visually checked at microscope.

3.2. Pulsed Laser Deposition

Pulsed Laser Deposition method (PLD) is widely used for thin surface layers, particularly for materials and combination of materials that cannot be processed easily by other methods [10 and 11].

The main reason of PLD progress is that materials having any complicated composition maybe transferred to a substrate without changing stoechiometric composition. Control of material stoechiometry in transfer between target and surface layer film is obtained either by working in vacuum, or using inert or reactive gases. Multilayer structures can be easily obtained, thickness of the layer being accurately controlled (0.1 nm).

Process of thin layer growth using PLD evolves in four successive steps:

1. action of laser beam onto the target;
2. dynamics of ablated material (target) – plasma expansion;
3. interaction between ablated material and a substrate having a controlled temperature;
4. nucleation and growth of the layer onto the collector (implant) surface.

Each step is important to control layer parameters, like stoechiometry, density, cristalinity, uniformity and roughness.

Energy of plasma species and distance between target and collector are important parameters which determine layer quality.

Temperature of substrate's surface has a determinant role in diffusion ability of atoms. High temperatures are favourable to rapid growth of crystals, but low temperatures or high saturation may perturb crystals growth leading to high disorder or amorphous structures.

Due to possibility of independent variation of many parameters, PLD is a versatile technique to obtain this layers with great diversity of morphological and structural characteristics [12–20].

All parameters can be controlled in order to optimize regime for obtaining structures and thin layers. Main deposition parameters are: wavelength, fluency, laser frequency, pulse duration, substrate temperature, area of laser spot, deposition geometry, nature and pressure of gas in deposition chamber.

If ablated material reacts with ambient gas composition of the layer deposed may be different from the target one. This is the case of Reactive Pulsed Laser Deposition (RLPD).

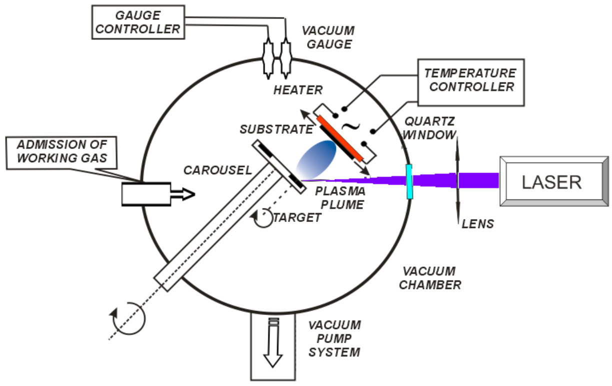

Fig. 6. General PLD equipment used in experimental research.

Growth of thin layers using PLD/RPLD method(s) has numerous advantages:

- laser source is external from deposition chamber, giving a great flexibility in material use, layer geometry and deposition parameters adjustment;
- most materials can be laser ablated;
- because of pulsed laser layer growth rate is accurately controlled (in fractions of angstroms);
- ablated material quantity is localized in plasma volume generated by laser pulse;
- in optimal deposition conditions stoechiometry of deposed layer is identical with the target's, even for complex and unstable materials
- high energy of ablated species leads to adherent obtained layers;
- new phases of material can be obtained.

General PLD research equipment used in our experiments (at National Institute for Lasers, Plasma and Radiation Physics) is presented in the following (Fig. 6). A laser pulse of great shine, generated by an excimer laser source KrF* (λ = 248 nm si τFWHM ≈ 25 ns), gets inside the reaction chamber through a quartz window. Energy of the laser pulse can be regulated in range of 10–700 mJ and it is monitored by a Coherent system. Duration of laser pulse is measured and visualized by an oscilloscope Tektronix 350 D.

Laser beam is focalized on the target surface by means of a cylindrical lens situated inside the deposition chamber. Incidence angle of the laser beam on the target surface is 45º. Before entering into the deposition chamber, the substrate is cleaned using an ultrasonic bath. During deposition target is rotated and translated in order to avoid punching, to efficiently use of the target surface and to obtaining uniform deposition films. As well, decomposition of target material because of multiple irradiations is avoided.

Heating and cooling processes are controlled with a temperature monitor device.

In order to avoid any contamination and to guarantee gas purity during deposition process, the reaction chamber is under vacuum of 10^{-4} Pa, using a high vacuum pump. Dynamic pressure of ambient gas is kept constant during deposition.

Before introducing in the chamber targets are cleaned by chemical methods. To avoid residual contamination before real layer deposition, 1 000 consecutive cleaning pulses are applied. During this phase, a screen is inserted between target and collector in order to eliminate initial ablated substance containing impurities.

In a deposition process several targets can be used, being made of the same material or different materials (in case of multi-layers.

The equipment has a carousel having the possibility to fix up to five targets, for deposing up to five different layers successively. Otherwise, opening the deposition chamber could lead to modifications of the layers' substances by means of oxidation or adsorption of molecules on the surface layer.

3.2.1. Experimental conditions / Laboratory technology. Quality and properties of surface layers obtained using PLD depends on the targets' characteristics. A compact and hard target having small roughness of surface will give good quality deposed layers by less defects and a reduced consume of target material.

In order to obtain compact powder targets of an imposed diameter a special mould is used on a hydraulic press.

More compact, stable and hard targets were obtained by heat treatment at high temperatures, restricted only by the melting temperature of the components. It was used sintering process in a Carbolite oven, which allow heating and cooling constantly, avoiding heat shocks that lead to cracks into target.

HA targets were obtained by pressing at 3MPa and sintering at 3800 ºC for 6 hours.

In the experiments were used laser pulses generated by excimer laser source KrF* (LambdaPhysik/Coherent Radiation COMPEXPro 205, λ = 248 nm and τFWHM ≈ 25 ns).

For the experimental prototype implants two sets of films were deposed.

For the first set, ZrO2:HA and β-TCP films were deposed on Ti substrates (discs having diameter of 3 mm), which were implanted in rabbits tibiae, respecting ethical issues in biological studies. Experimental PLD conditions were as presented in Table 2. All depositions were made using a laser pulse frequency of 10 Hz.

For second set HA, βTCP and bioglass layers were deposed on threaded prototype dental implants. These implants were also inserted in rabbit tibiae, respecting ethical research issues.

Table 2

PLD conditions for thin films of ZrO2:HA and β-TCP on disc prototype implants

Target	T (°C)	Distance target-substrate (cm)	Pressure (Pa)	Energy (mJ)
ZrO2:HA	450	4.5	50	470
β-TCP	400	4	13 (O2)	235

Table 2 (continued)

Target	Spot (mm^2)	Fluency (J/cm2)	Number of pulses	Heat treatment after deposition
ZrO2:HA	8.12	5.79	10.000	Vapours H_2O, 6hrs
β-TCP	9.42	2.49	10.000	Vapours H_2O, 6hrs

Table 3

PLD conditions for thin films of ZrO2:HA and β-TCP on threaded dental prototype implants

Target	T (°C)	Distance target-substrate (cm)	Pressure (Pa)	Energy (mJ)
HA	450	4	45	500
Bioglass 6P57	400	4.5	13 (O2)	150
β-TCP	400	4	13 (O2)	235

Table 3 (continued)

Target	Spot (mm^2)	Fluency (J/cm^2)	No. of pulses	Heat treatment after-deposition
HA	9	5.56	10.000	Vapours H_2O, 6hrs
Bioglass 6P57	8	1.88	10.000	Vapours H_2O, 6hrs
β-TCP	9.42	2.49	10.000	Vapours H_2O, 6hrs

As in previous case, all depositions were made using a laser pulse frequency of 10 Hz

After deposition, all samples in both sets were treated in water vapours for 6 hours. During this treatment the samples were heated at same temperature as the one used during deposition. Role of after deposition treatment is to maintain stoechiometry of the surface layer and improve crystals of covered substance.

Main disadvantage of PLD is manufacturing cost, meaning high cost of the equipment and the fact that it is meant for research, not for production.

4. TYPES OF REAL DENTAL IMPLANTS

There are two main types of threaded dental implants: in one step and in two steps.

4.1. One step dental implant

This one step means the implant can be and it is really used after implantation. Generally, these implants are orthodontic (Fig. 7).

As seen in Fig. 7, dental implants have threaded sandblasted surface.

4.2. Two steps dental implant

These usually threaded dental implants imply two phases (steps) – see Fig. 8:

Fig. 7. Orthodontic dental implants.

Fig. 8. Two steps threaded dental implant.

1. dental implant screw insertion, followed by healing period (see Fig. 8, lower element);
2. upper structure assembly, meaning dental crown fixed on dental screws with fixing screws and abutments after healing period (see Fig. 8, middle and upper elements).

5. CONCLUSIONS

After several years of research and manufacturing of dental implants some conclusions can be underlined:
- base structure materials for dental implants and maybe not only for dental implants are titanium and zirconium, which are similar metals from the chemical point of view, inert to human body fluids, together with their alloys;
- there could also be used as base structure materials alloys between titanium and zirconium;
- own research related to surface layers materials leads to the conclusion that naked titanium and titanium alloys implants are as good as surface layered titanium implants, meaning TiO_2 is at least as good material for surface layer as other materials like HA, βTCP, bioglass. TiO_2, occurring naturally, is not a necessary supplementary manufacturing process to obtain the surface layer, not implying additional costs to the implants;
- PLD is a real method to obtain submicronic surface layers onto dental implants, but it has high cost. It is used actually only in laboratory (research) technology;
- the cheapest method to obtain necessary micro geometry of implants surface is sandblasting with 250μm diameter of sand granule.

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