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Analysis and possibility of modifying the properties of the Ti6Al4V titanium alloy via the method of the preparation for the use in a dental implant

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ABSTRACT

Purpose: In the given paper the analysis of the Ti6Al4V alloy has been carried out, methods for manufacturing of components for use in dentistry as well as the impact on the human body have been described. Then the controversy over the possibility of modifying the properties of a final product - an implant by the use of the injection method not used so far in that field has been taken.

Design/methodology/approach: Titanium alloys in dental application should be characterized by high corrosion resistance and biocompatibility. In the framework of the given paper the commercial methods of the production of titanium elements for biomedical applications have been analysed.

Findings: In the framework of the analysis of the possibilities of changes in the properties of the Ti6Al4V titanium alloy, the injection method for the production of a finished product - an implant, so far not used for a commercial scale, has been proposed.

Practical implications: In practice, the application of those considerations will find the representation in further researches carried out by the possibility of using the injection method to modify and improve the mechanical and physico-chemical properties of the final product. An important aspect is the fact that during the modification of the manufacturing process the chemical composition of the alloy out of which the implant will be produced, will not change.

Originality/value: The fact of taking the controversy over the possibility of using the injection methods for the production of dental implants, also for an industrial scale is an original aspect in that consideration.

Keywords: Dental implants; Ti6Al4V; Titanium

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MATERIALS

1. Introduction

Thanks to series of researches many physicochemical and biological properties of titanium are known. Those studies led to the specific breakthrough in the field of biomaterials and biomedicine. Through the application of numerous clinical observations which have been focused on the biocompatibility and capacity of osseointegration, titanium and its alloys have been started to be used for the production of elements and also all sets used in modern medicine - both surgery and aesthetic medicine [1].

Already in the 1940s there were the first attempts of the use of titanium in implantology because it showed high corrosion resistance as a result of the formation of a tight and durable layer consisting mainly of titanium dioxide (TiO_2) [2]. That ability is of the paramount importance in the use of those materials within a living organism. Nethertheless, essential problems concerning titanium itself appeared. Taking into consideration those incovenieces researches concerning the improvements of those properties which were improved by creating alloys began to be carried out - in the 1960s titanium alloys with vanadium, in particular Ti6Al4V made the running. That alloy found its application mainly in orthopedics (knee and hip replacement, and also in traumatology) [3].

Satisfaction with vanadium titanium alloys did not last too long, what resulted from an appearing report about the toxic effects of vanadium on living organisms. As a result of those premises in the 1980s the work on new kinds of biomaterials based on titanium - without vanadium, began to be carried out. A nickel titanium alloy (nitinol) with shape memory which comes back to the previously remmebered shape in the temperature of human body can be mentioned as an example and that property is used for orthodontic arches, surgical clamps or stents. Through a series of improvements and the outworking of the structure β of titanium alloys, titanium-based biomaterials are at the top of metallic biomaterials [4-6].

Summing up, titanium with its alloys against the background of other metallic materials is characterized by incredible biocompatibility, the lowest Young's Modulus, the ability to self-passivation affecting the corrosion resistance, high heat resistance (800°C) and high relative strength (1800 MPa) while low specific density [7,8]. However the largest drawback of the use of those materials is the problem of its treatment needed to achieve the final end product - the implant.

2. Description of the approach, work methodology, materials for research, assumptions, experiments etc.

2.1. Characteristics of titanium

Titanium exists in two allotropic forms - α which is stable to the temperature of 882°C crystalizing to A3 hexagonal network (constant network: a = 0,2951 nm, c = 0,4679 nm, c/a = 1,587 nm) and β which is stable over 882°C to a melting point of titanium that is 1668°C crystalizing in A2 network - regularly centered (constant network of 900°C a = 0,3306 nm) [9]. Density of titanium is changed from 4.4 g/cm^3 ± 0.1 g/cm^3. technical titanium is the most widely used in a medical aspect and its four types (depending upon % oxide content) are distinguished [10] (Table 1), what is associated with specific concentrations of carbon values, oxide, nitrogen and iron. Due to problems involving the exact determination of the gas concentrations in technical titanium its classification is carried out on the basis of mechanical properties (Table 2) [1] - particularly strengthening under the influence of cold working is noteworthy. Its best example is the production of cold moulded titanium rods in the annealed condition equalling about 420 MPa, and after 85% - deformation it increases to ~865 MPa, in order to eliminate the effects of density recrystallization annealing in the temperature range of 600-700°C. When selecting the conditions in which plastic deformation takes place its specific properties should be taken into consideration:

- a high yield point similar to that of the tensile $R_{0,2} / R_m = 0.79\text{-}0.92$,
- susceptibility to deformable and allotrophy,
- very high chemical reactivity with atmospheric gases at temperatures of 120°C.

Such acids as: sulfuric, hydrochloric, phosphoric, fluoro formic, oxalic, trichloroacetic have influence on the titanium. Titanium itself has very good resistance to corrosion, which has total resistance for wet chlorine, hypochlorous acid, chlorine dioxide, chlorate brine and chlorides and its solutions (KCl, $BaCl_2$, $FeCl_3$, $ZnCl_2$, $MgCl_2$, NaCl, NH_4Cl), also shows resistance to sulfides, sulphureous and sodium hypochlorite in a wide range of temperature and concentration. In addition, titanium is resistant to sea water, ammonia, nitric acid, molted sulfure, hydrogen sulfide, hydrogen peroxide. Moreover, it is also resistant to pitting intercrystalline and stress corrosion.

Table 1.
Chemical composition of types of titanium (C_p) and its exemplary alloys [11]

	C_p (Grade) I	C_p (Grade) II	C_p (Grade) III	C_p (Grade) IV	Ti6Al4V	Ti6Al4V ELI
N	0.03	0.03	0.03	0.03	0.05	0.05
C	0.10	0.10	0.10	0.10	0.08	0.08
H	0.015	0.015	0.015	0.015	0.015	0.012
Fe	0.02	0.03	0.03	0.05	0.30	0.10
O	0.18	0.25	0.35	0.40	0.20	0.13
Al	-	-	-	-	5.50-6.75	5.50-6.50
V	-	-	-	-	3.50-4.50	3.50-4.50
Ti	rest	rest	rest	rest	rest	rest

Table 2.
A summary of certain mechanical properties of materials used in implantology as indicated by ASTM compared to human hard tissues [11]

Material	Density [g/cm^3]	Limit strength [MPa]	Young's module [MPa]	Tensile strength [MPa]	Elongation [%]
Cp I Ti	4.5	170	102	240	24
Cp II Ti	4.5	275	102	345	20
Cp III Ti	4.5	380	102	450	18
Cp IV Ti	4.5	483	104	550	15
Ti6Al4V	4.4	860	113	930	10
Ti6Al4V ELI	4.4	795	113	860	10
Co-Cr-Mo	8.5	450	240	700	8
Stal 316 L	7.9	690	200	965	20
Bone	0.7	Bd	18	140	1
Dentine	2.2	Bd	18.3	52	0
Enamel	3	Bd	84	10	0

2.2. Characteristics of titanium alloy

Titanium and its alloys, depending on the chemical composition may incicate in its morphology several types of structures - monophasic structure α and β or biphasic structure α+β. In spite of those phases there are also two other phases - pseudo α and β. Each of those structures has its own characteristics which is associated with the amount of a given phase [12]

In the case of a monophasic structure α very good corrosion resistance, high weldability, significant fracture toughness and creep resistance - much higher than for alloys containing a significant advantage phase β are observed.

Despite of those advantages, alloys with strucutre α have lower strength and flexibility as compared to the alloys with phase β. There is the possibility to oppose to plastic forming defects of those alloys through increasing the processing level it concerns particulary for alloys with high content of aluminium. When phase β appears in phase α in the amount to 5% those alloys are called pseudo α, which are in its characteristics with significantly improved creep resistance and resistance to high temperatures. To the stabilization of that phase elements which increase the transition temperature α ↔ β including Al, Ga, Ge, oraz N, C, O [13] are used. An example of a single-phase alloy α is Ti5Al2, while pseudo α - Ti8Al1Mo1V.

Alloys, which have the structure of phase β and pseudo β, are the ones with properties similar to the alloys with structure α+β with significant amount of phase β, which after normalization has strucutre composed of a metastable phase β_M; however it is needed to have in mind the fact that in the pseudo β structure there is also significant amount of phase α. Alloys with structure β show high strength properties, better combination of strength and fracture toughness, deeper volume heardenability, and very good properties allowing for plastic deformation. In addition alloys with that phase thanks to the high solubility of hydrogen has fairly good corrosion resistance. Along with a significant amount of concentration of hydrogen hybrids are formed. In contrast to the alloys with phase α in alloys with phanse β a significant increase of production costs is observed. Alloys with phase β have increased density ~ 5 g/cm^3. Both elements (the price and density) are caused by the mass density of alloying elements and their price. In order to stablize that phase, such elements which lower the temperature of the allotropic transformation α ↔ β as are used:

- isomeric elements V, Mo, Nb, Ta,
- eutectoid elements Cu, Cr, Mn, Fe, Ni, Co, Si,
- pseudo isomorphic elements Ru, Rh, Re, Ir,
- elements that do not stabilize any phase - neutral elements Zr, Hf, Th, which are added because of solution-strengthening effect, as well as the occurrence of phase transformation, which causes the formation of a fragile metastable phase ω [14].

An example of a single-phase β alloy is Ti10V2Fe3Al while example of pseudo β is Ti8Mn.

Besides single-phase structures, there are also two-phase structure α+β which consists of 10-50 % phase β at room temperatue conditions (25°C) and the achievements of two-phase structure relies on adding elements to the phase α. It is necessary to remember that phase β stabilized by eutectoid elements shows low stability and, as a result of slow cooling may disintegrate in the following manner: $\beta \rightarrow \alpha+\gamma$. The additive, which is used to stabilize and strengthen phase α is aluminium which allows for the growth of thermal stability at the same time the reduction of the density of the alloy. In case of elements stabilizing phase β there is impact on mechanical properties of the whole alloy. Isomeric elements cause an increase in ductility, and decrease of the tensile strength of the phase β, but eutectoid elements generate the opposite effect to the mentioned above. Dual-phase alloys α+β have high plasticity, corrosion resistance and strength [13,15].

As a result of observation it was noticed that the growth of phase fraction β improving the mechanical properties of the entire two-phase system α+β where the maximum is achieved in the case of distribution phase 50-50 (Fig. 1) [16]. The disadvantage of such a system is a decrease of phase alloy formability, however it may be enforced by heat treatment. Among alloys having such phase distribution there is mentioned ealier Ti6Al4V alloy [13,15,17]

In order to illustrate better the individual properties of single-phase alloys α and β, as well as two-phase alloys α+β the table containing some properties (Table 3) which were evaluated on the basis of that scale was prepared:

- mediocre (1),
- poor (2),
- sufficient (3),
- moderate (4),
- good (5),
- very good (6).

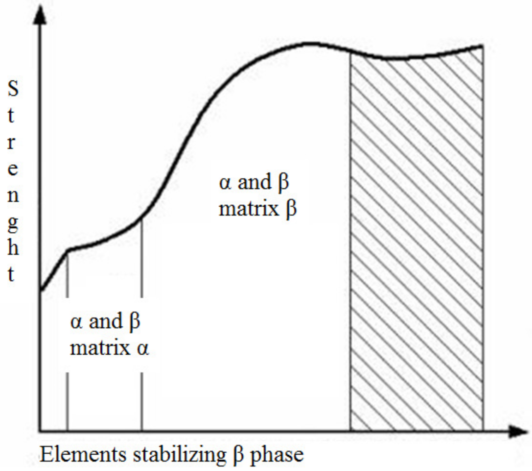

Fig. 1. Effect of the phases on the mechanical properties of the alloy [16]

Table 3.
Comparison of properties of single-phase α and β and dual-phase α+β of titanium alloys [13]

Properties	Titanium alloy		
	A	β	α+β
Strength	2	6	5
Density	5	2	5
Fracture toughness	5	4	3
Corrosion resistance	6	4	5
Oxidation resistance	6	2	4
Cold formability	1	3	2
Weldability	5	2	4
Plasticity	3	4	5
Creep resistance	5	2	4

2.3. Titanium as dental biomaterial

Titanium in dentistry was initially used in the form of finished manufactured goods, among which implants, root canal studs and around the pulp studs can be mentioned. Thanks to the development of technology a number of possibilities for the production of titanium elements of the prosthetic constructions - crowns, bridges, partial dentures skeletons, telescopic crowns, mesostructure and suprastructure implant constructions appeared [18,19]. The wide application of titanium in terms of, not only dental and general medical aspects is thanks to the discovery of osseointegration by Brånemark in 1965 [20,21] Thanks to those features, the titanium allows for the contact buildup of a bone so called contact osteogenesis. In the histological image (Fig. 2) healing of implants made of titanium is carried out in a manner virtually identical to the restoration of a bone wound. However they may appear slight inflammatory reactions related to the intrusion of a foreign body in a living organism. The phenomenon of osseointegration is used in prosthetic dentistry to rebuild the missing teeth by implanting titanium intra-osseous implants as pillars of the different types of dentures [6].

Since that discovery the number of implants in the world including in Poland has increased in proportion to the wealth of the society and the number of doctors - dentists who are authorized to perform implant surgery.

As a result, there are newer evidence on clinical observations, including rare descriptions of various body response to titanium and its alloys. In the context of those observations it is noticed that materials such as titanium, as well as other alloplastic materials may cause various defensive reactions including rejection of the implant, but those reactions are observed much less frequently than in the case of transplantation.

Titanium is regareded as a biocompatible material when it is not a reason for the appearance of a pathological reaction in tissues, it does not emit any substance which leads to the disintegration and in the case of intra-osseous implants allows for the growth of a bone directly on the surface of the implant [22].

A number of factors that are associated both with the material itself, surgical technique as well as the state of the tissue surrounding the side of the implant are responsible for the phenomenon of osseointegration [23,24] The construction of implants, their shape, the choice of suitable parameters such as length, width (Fig. 3) primary stability and endostial surface have a significant impact on the duration of their usebility [25,26]. The developmentof technologies for surface engineering allows for an endosteum part of the implant for much better proliferation of osteoblasts and implant covering by a hydroxyapatite jacket improving primary and secondary stability [27].

A type of the implant and its resistance to corrosion significantly increases the success of the long term use of implant which results in comfort [29]. Besides titanium, metals having affinity for tissues are niob and tatalum. At first it was thought that titanium by its corrosion resistance gains thanks to the formation of oxides on the surface. However along with clinical trials it was found out that despite the passive action of oxides covering the implant in the mouth electrochemical and galvanic corrosion leading to the release of titanium ions into the surrounding tissues can occur. Favorable reactions with body fluids and their salts that form the phosphate-containing and calcium-containing hydroxy groups can be observed there. That is why it is so important to combine titanium with other elements improving its corrosion resistance.

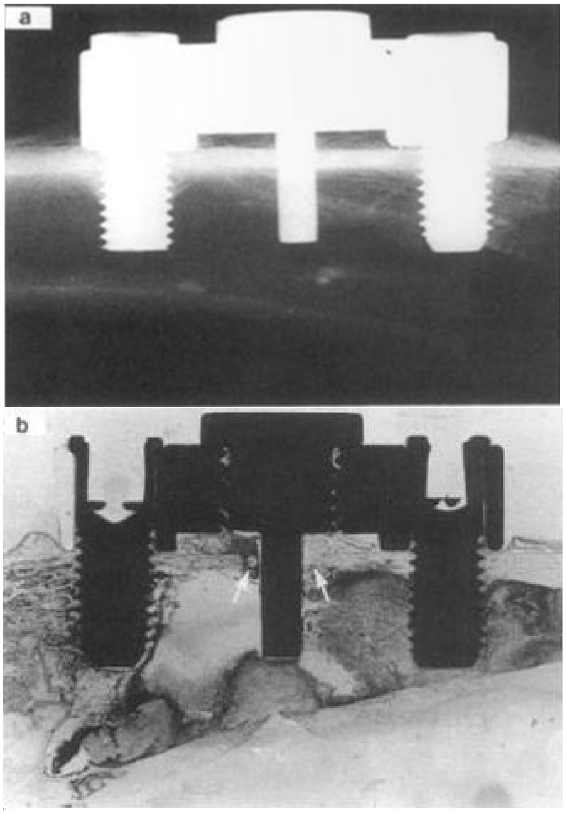

Fig. 2. Radiograph (a), and clipping the surface of the implant made of pure titanium (b). In place of the arrow a histological image where the implant is covered with a thick layer of a bone tissue can be seen [28]

Fig. 3. Examples of implants

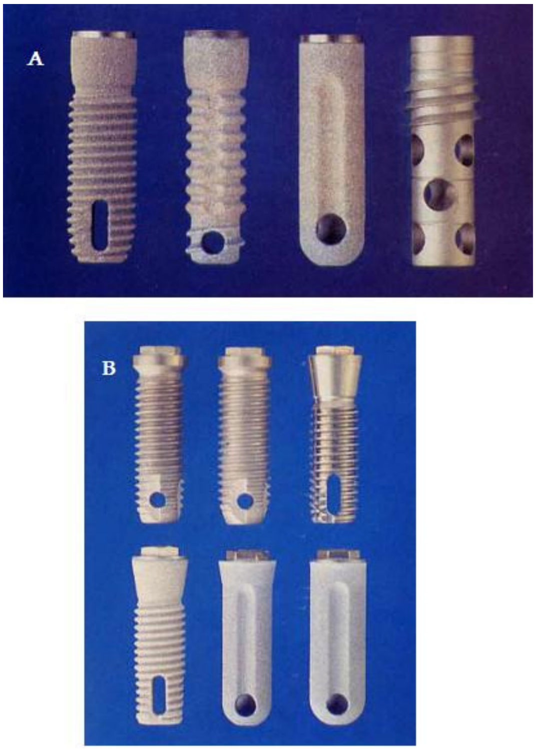

Fig. 4. Examples of implants with internal hex (a), and external hex - (b). In the Figure A from left: Screw-Vent, Micro-Vent, Bio-Vent, Core-Vent. In the Figure B from left: Swede-Vent Standard Implant, Swede-Vent Conical, Self-Tapping implant, Bio-Vent X Cylinder Implant [30]

3. Description of achieved results of own researches

Although titanium metal is relatively inexpensive and commonly occurs in the earth crust, it does not belong to the materials that are used on a very large scale - what is associated with the high costs of processing. The most commonly used methods for titanium processing for dental prosthetics are:

- casting process,
- spark erosion,
- milling finished blocks of CAD/CAM method [31].

The basic laboratory method of processing metals and their alloys, which are used in dentistry is casting. However, having taking into consideration titanium and its properties - high melting point, low specific gravity, high affinity for oxygen, carbon, hydrogen, nitrogen and silicon at elevated temperatures, the process is very complex and generates many problems [32].

The most commonly used system in titanium casting is the pressure - vacuum system in the system of two chambers. The top chamber is equipped with a copper crucible, whereby means of the arc titanium is melted, while the lower chamber is equipped with a ring with the casting mold. From both chambers the air is pumped out and then to the upper chamber precious gas - helium or argon is introduced. In the lower chamber there is vacuum, then injecting of the melted titanium to the form due to the pressure in the upper chamber, which also favors the vacuum in the bottom chamber. In order to evenly melt many devices are equipped with a circulating arc, which turnovers result from changes of the magnetic field. During titanium casting separators are not used as it is used in practice in the case of gold, which is associated with low specific weight of titanium; in foundry using centrifugal force, centrifugal forces allows to fill the empty mold with liquid metal are directly proportional to the density of cast metal. So in order to achieve the same result - using centrifugal forces - as in the case of gold, the centrifugal force should be four times greater for titanium [33]. Therefore, when performing solid titanium prosthesis it is recommended to model crown walls slightly thicker than the analogous additions produced on the basis of other metals, the thickness shall not be less than 0,5-0,6 mm, in the case of crowns of metal or gold base, that range fluctuates around 0,3-0,4 mm. As a result of too “thin” modeled titanium errors such as a perforation of the crown walls or the lack in refill of the periphery which affects the lack of usefulness of casting can occur.

Because many difficulties occur in the casting process of titanium, alternative treatment methods of the metal - the spark erosion and CNC milling have been implemented [1].

Spark erosion is a method of erosive treatment on elements made of titanium such as plates, dentures, crowns, bridges, or intraosseous implants. The processing of titanium in such a way eliminating the stress in the material that arise as a result of CNC machining using cutting tools. By using electro-erosion it is possible to manufacture very small elements of prosthetic constructions, and items of complex geometry (hardness of material afected on accuracy), rough surface where the production of those elements by other methods of waste machining for example cutting would be practically impossible.

The process itself consists of voltage applied between the electrode and sealed workpiece which results in heterogeneous time-varying electric field (10^5-10^6 V/cm. The material during machining is immersed in a dielectric liquid - oil or deionized water. With sufficient intensity of an electric field and voltage border electrical breakdown appears, as a result emission of electrons from the cathode is observed. A place, at which the largest electric field operates, is characterized by a concentration of pollutants in the dielectric. Dielectric particles are given into the ionization during which the plasma channel is created around which a blister of gas is formed. Electrons emitted by the working electrode hitting the surface of the workpiece cause the heat generation, the local increase in temperature causes progressive and intense evaporation of material (Fig. 5). The process is characterized in such a way that it proceeds in the form of explosions where the collected material realesed into the dielectric, after the process a gas bladder and closes implode - which facilitates the removal of processing products [34] (Fig. 6).

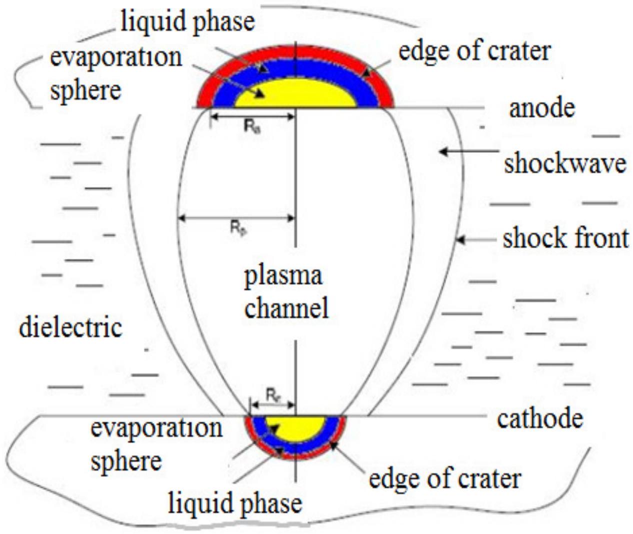

Fig. 5. Electrical erosion model, taking into account the temperature distribution [35]

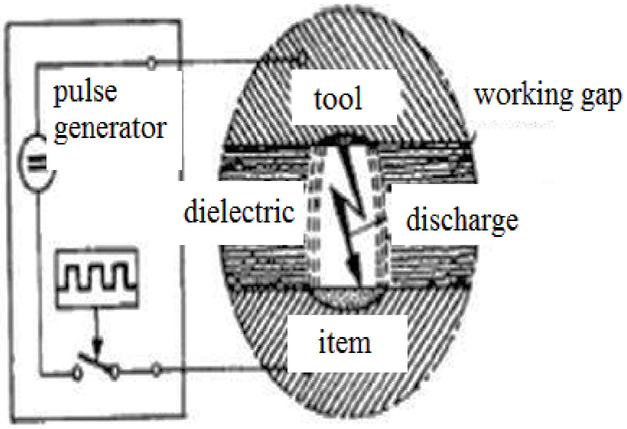

Fig. 6. Remove surplus of material [35]

The last of the most widely used titanium processing methods is the use of CAD/CAM in CNC technologies. Thanks to proper software and machines with the appropriate tolerances titanium blocks can be produced by milling process. That method is one of the most advanced methods that are used in the manufacturing of dental restorations in dentistry [36]. The whole process starts with extrusions taken by a dentist whih are transfered to a dental technician, whose task is to cast a model. Such a pre-model should be performed according to requirements set by the CAD/CAM system to transfer data from the pillar of the model in the scnaning to the system. After analyzing the optical scanner models (a light or laser) or mechanical, photographic data obtained in that process are transferred to the computer. The next step is to design a computer image of the substructure - its thickness, size and range spans of the bridge, shape and sculptures of the occlusal surface, then data are sent to a CNC machine. CAD/CAM system allows to perform additions with incredible precision by using the most accurate CNC machines, supplement manufactured with that technology have developed an exact match to the pillars, where marginal seal of such additions is below 100 microns [37]. The disadvantage of the system is the high cost of equipment, complicated modeling technology and preparation of items, the dependence of product quality on hardware, the need to equip the laboratories with specialized equipment [38].

In addition to the above mentioned disadvantages there are a number of technological problems due to the treatment of titanium, the cutting is difficult because the strong chemical affinity is observed to materials out of which the tools are made, it is a high tendency of the adherence of material to cutting tools, low thermal conductivity which causes the concentration of heat on the cutting edge of tools and blades which generates temperatures to 1100°C resulting in the reduction of tool life and their deformation resulting in geometric imperfections of the workpiece. Additionally, titanium has high strength which during cutting is problematic, the strength depends on the cutting speed, where speeds are different for pure titanium, which is relatively soft or for hard alloys β.

4. Conclusions

Taking into consideriation the above mentioned reasons, it is clear that there is a need to make the most efficient and cost-effective production of titanium components for the dental implant. From a technological point of view, one should strive for a solution which will eliminate most problems related to the processing of titanium, which appear irrespectively of the production method.

One alternative - so far unused on a commercial scale - is the production of elements using the method of injection casting. That method makes it possible to reduce production costs through the possibility of multiple, rapid repetition of the cycle in a very short period of time and allows for the control of virtually every parameter responsible for the possibility of processing various titanium alloys.

As a part of the pre-work carried out within the possibilities of using the injection method the possibility of replacing commercially methods by injection casting method is clear. In addition, preliminary studies indicate the possibility of improving the properties of alloys by modifying the surface layer during the process of creating the final product, a process which in fact allows to obtain a finished product from ingots virtually in a single technological step.

Additional information

Selected issues related to this paper are planned to be presented at the 22nd Winter International Scientific Conference on Achievements in Mechanical and Materials Engineering Winter-AMME’2015 in the framework of the Bidisciplinary Occasional Scientific Session BOSS'2015 celebrating the 10th anniversary of the foundation of the Association of Computational Materials Science and Surface Engineering and the World Academy of Materials and Manufacturing Engineering and of the foundation of the Worldwide Journal of Achievements in Materials and Manufacturing Engineering.

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