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Innovative Technology To Achieve Some Multi-Purpose Surgical Implants, Biologically Active

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The aims of paper consist to present the results of experiments conducted within the Project 71-080 unfolded as part of the 2nd Romanian National Research Programme-NCMP, which resulted in obtaining some materials with high quality characteristics, which should lead to obtaining products of complex geometry and improved chemical-structural features by metallurgy technologies, meant to be used in the medical industry. The paper presents the physical-chemical, mechanic and structural features of the composite materials of Ti6Al4V and Ti6Al7Nb alloys. Often Ti6Al4V alloy is used like implant material, but at the present due to the toxicity of vanadium his use is restricted. For this reason a Ti6Al7Nb alloy was also processed.Ti6Al7Nb is less corrosive than Ti6Al4V alloy and from this point of view Ti6Al7Nb alloy seem to be very close with pure commercial titanium. There are presented in a detailed manner the possibilities to realize some TiNO/ZrNO thin films deposits on Ti6Al4V/ Ti6Al7Nb alloys support by a new PVD technique which suppose a combined magnetron sputtering and ion implantation (CMSII).

1. Introduction

Biomaterials are a class of special materials possessing good mechanic properties that once implanted in the living body do not have side effects (or these effects are minimum) in contact with the biological tissues: blood, cells or proteins[1,2].

The properties and functions of biomaterials are frequently approached in the context of the endo-prothetic implants since they are used for the beneficiary's entire life span. Theoretically speaking, the attractive mechanic properties of titanium and its alloys, including its reduced weight, the ratio resistance-weight, its high ductility and the low thermal conductibility allow the design modifications in the fixed and mobile prostheses having as a result a comfortable functionality and use [2, 3].

The physical-chemical and biological characteristics necessary for a material used in osteosynthesis implants are: ►biocompatibility with the bony tissue; ►exceptional physical-mechanical characteristics; ►high mechanic resistance associated to low density; ►low dilatation coefficient at temperatures between 20 – 50°C; ►low elasticity module; ► corrosion resistance; ►resistance to organic acids;

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►resistance to alkaline solutions and chlorides; ►chemical composition of high purity; ►low gas contents (H, O, N).

All these characteristics imposed to a biocompatible material are met to a large extent by titanium and the Ti-based alloys with applications in odontology, orthopedics and cardiovascular surgery. The biological characteristic of Ti relies on the existence of the TiO_2 layer forming in environments containing oxygen. This oxide film is stable for different pHs (what gives it a remarkable resistance to easily reducing environments, neutral and very oxidizing) and to quite high temperatures. Only in conditions with very high reducing potential may there occur the breaking of this TiO_2 film and may appear the corrosion phenomenon, a phenomenon almost impossible to produce in the oral cavity or the human body. [2] Titanium may be alloyed with different elements to improve the mechanical properties (mechanic resistance to high temperatures, stretch resistance, the response to the wear thermal treatments, solderability and deformability.

The titanium alloys α-β have a good mechanic resistance due to the structure of the duplex phase. The most known titanium alloy α-β is TiAl6V4. Though the alloy TiAl6V4 is widely used in odontology, studies have shown that the release of aluminum and especially of the vanadium ions from the alloy may cause long term problems such as the peripheral neuropathy, osteomalacia and Alzheimer disease [4]. For this reason, they tried to find new technical solutions to make other alloys based on titanium such as TiAl6Nb7, considered to be an almost perfect substitute of pure Ti and of TiAl6V4.

2. Geometry of implants and semi-product sizes

The typo-dimensional diversity attained due to the improvement of the technologies of elaboration, casting, deformation and processing of the pure titanium and its alloys allow the oral surgeon to choose the type of implant that fits best the clinical problem analyzed following a complex clinical radiological exam.

From the viewpoint of the depth of the prosthetic field for implantation, implants may be: ►subperiosteal; ► intrabony;

The application of the subperiosteal implants is limited due to the frequent failures and the serious destruction of the prosthetic field at the moment of removing the implant.

As for the constructive shape, implants may be: ►cylindrical (the most used); ►conic; ►spiral; ►acicular; ►blade type (flat); ►tuning fork type;

In **figure 1** we present different dental implants with diverse geometries and different shapes.

Fig. 1 – Typo-dimensional variants of the dental implants [4]

To make the implants we chose two constructive solutions: 1) classic implants of the Branemark type (figures 2,a,b); and 2) implants made after one's own conception (figure 3).

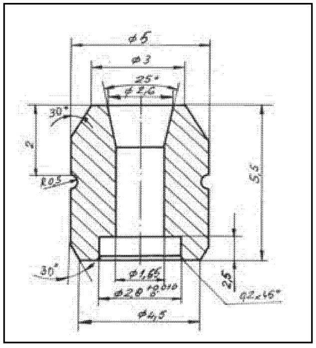

Fig. 2 a - Branemark prosthesis support

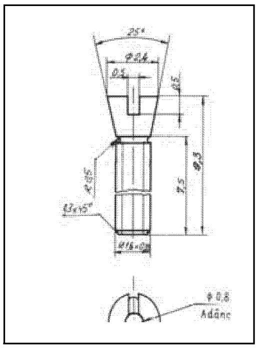

Fig. 2 b - Branemark fixing Screw M 1.5

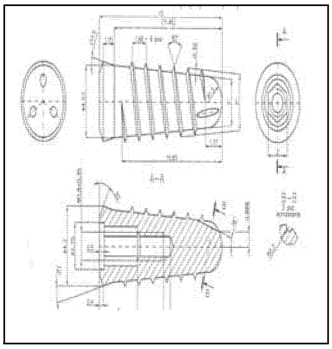

Fig. 3 - Implant

3. Making Of An Experimental Model From Biocompatible Material

The physical-mechanical, chemical and structural characteristics as well as the high biocompatibility of pure Ti and its alloys Ti6Al4V respectively Ti6Al7Nb involve the need to know well the technological particularities for the entire fabrication flow. Without the detailed knowledge of these particularities we cannot obtain materials with high biocompatibility, high resistance characteristics and what is most important, the manner of elasticity as close as possible to the one of the human bone.

The technological stages to make the experimental methods are:

1	Raw material	- Ti sponge - pre-alloys Al, V, Nb, TiO_2
2	Electrode making	- lab level: pressing by mould with the tightening angle of 22°
3	Melting-remelting	- lab level: vacuum arc remelting on Leybold-Haeraeus installation - number of remelting: at least 2
4	Ingot cutting off	-one shall cut off clean the ends and lateral surface of ingots -turning shall be exe-cuted in the conditions described in the previous chapter - one shall take samples for the chemical analysis
5	Non-destruc-tive control	- is made by ultrasounds
6	Protection of the heating surface	-ingots shall be covered with a thick layer of Na silicates mixed with calcium lime (CaO)
7	Heating for deforming (forging)	-the heating temperatures shall be: - for pure Ti: 900°C - for Ti6Al4V: 980°C - for Ti6Al7Nb:1080°C - maintenance period: 1h/0.7 inch;
8	Forging	-is made by hydraulic press of at least 1600tf -final size: 150 mm - number of heats: 4 -reduction by passing: 25 mm

		- temperature of final forging: - for pure Ti: 750°C - for Ti6Al4V: 800°C - for Ti6Al7Nb: 900°C - cooling in calm air
9	Intermediate thermal treatment	- is made on roller-hearth furnaces - maintenance temperatures: - for pure Ti: 700°C - for Ti6Al4V: 780°C - for Ti6Al7Nb: 820°C - plateau period: 4h - cooling is made in air
10	Exfoliation operation	- exfoliation is made from Ø 140 up to Ø 130 mm
11	Hammer forging	- is made by pneumatic hammers up to the diameter of Ø 45 mm
12	Intermediate thermal treatment	- softening treatment effectuated with the parameters described at point 9
13	Exfoliation	- is made on exfoliating machines or parallel lathes with high debit of cooling agent
14	Radial forging or hammer forging	- radial forging is made on semi-hot hammer-wrought installations with reduction by passing of max. $\varepsilon = 20\%$ per section - 250 kg hammer forging up to a 7 mm square
15	Softening thermal treatments	- are made on roller-hearth furnaces -maintenance temperatures: - for pure Ti: 700°C - for Ti6Al4V: 780°C - for Ti6Al7Nb: 820°C - plateau period: 4h - cooling is made in air
16	Mechanical processing by pressing and chipping of the Ø5mm bars	- the chipping processing is made to obtain thread and the final sizes according to the execution drawings from figures 2, 3.
17	Implant degreasing	- is made with tetrachloroethylene, ethylic alcohol and finally ultrasonic washing
18	Final thermal treatment	- is made in ovens with protection atmosphere - additionally they execute a de-tensioning treatment at 300-375°C
19	Surface conditioning	- is made by sand-blasting or plasma treatment, followed by covering by TiNO to increase biocompatibility
20	Sterilization	- is made by gamma radiations after packing in specialized units

4. Establishing the technological parameters to make the thin complex layers of titanium oxide and/or titanium oxynitride

They selected two new types of superficial layers, namely TiNO, ZrNO, so as to develop them. We must mention that by increasing density of ionic links, once with the increase of oxygen concentration we also determine the decrease of micro-hardness of the deposited layer. The option to create biocompatible layers from oxynitrides and not from oxides is determined partially by this behavior as well as by the higher resistance of these oxynitrides to mechanic shock, besides an increased adherence to metallic sublayers. The settling sown of the Ti and Zr oxynitride layers by reactive magnetron pulverization is made by pulverization of a metal target in an argon and reactive gas atmosphere.Within the cover technology there are two main stages:

Sublayer preparation focuses on the cleaning of sublayers for settling down, a preparation referring both for the cleaning (by chemical and physical processes) in the exterior of the technologic precinct (polishing, degreasing in ultrasound bath with organic solvents) and the pulverization by bombardment with medium energy ions (1000–7000 eV) in the technological precinct by application on sublayers of a potential of 1000V–3500V from a high voltage source in direct current.

Settling down of cover layers is made in the technologic precinct abiding by the technologic parameters: ►temperature in sublayer area <350°; ►gas total pressure: $3\text{-}5\text{x}10^{-3}$ mbar; ► nitrogen mass debit: 10 - 14 cm^3/min; ► oxygen mass debit: 1 - 4 cm^3/min; ►argon mass debit: 28-32 cm^3/min; ► settling down duration: 60 - 90 min.

4.1. Characterization of obtained layers

Element analysis of settled down layers

Element composition was determined by electron spectrometry method Auger - AES, using a spectrometer of PHI Model 3017 type. In *Table 1* we give the concentrations of every type of layer obtained.

Layer	Ti	N	Zr	O
TiNO	47,5	22,8	-	29,7
ZrNO	-	24,3	46,6	29,1

Table 1 Element composition of the investigated layers determined by AES

In figures 4 and 5we illustrate an AES spectrum for a part covered with TiNO respectively with ZrNO.

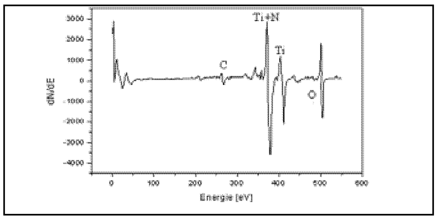

Fig. 4. AES spectrum for a TiNO layer

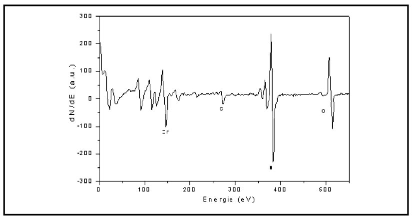

Fig. 5. AES spectrum for a ZrNO layer

The average thicknesses measured for the TiNO and ZrNO layers are given in *Table 2*

Layer	d (μm)
TiNO	2,3
ZrNO	2,1

Table 2 Thickness of settled down layers

Microstructure, morphology and surface topography of the settled down layers were investigated by AFM microscopy. In **figures 6** and **7** we present images of the layer surfaces of titanium oxynitride and zirconium oxynitride settled down on Ti6Al4V test bars. We may notice the formation of a uniform structure. In **figures 8** and **9** we present the images of the same layers after the thermal treatment in oxygen flow.

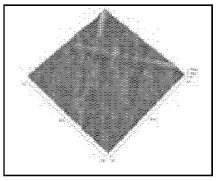

Fig. 6 - AFM image of the surface of a TiNO layer

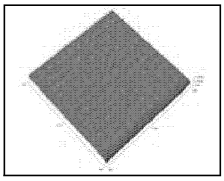

Fig. 7 – AFM image of the surface of a ZrNO layer

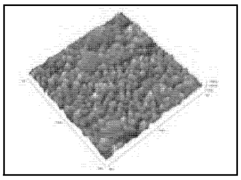

Fig. 8 - AFM image of the surface of a TiNO layer after thermal treatment in oxygen flow

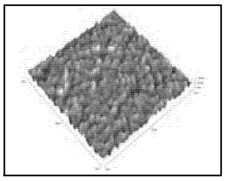

Fig. 9 - AFM image of the surface of a ZrNO layer after thermal treatment in oxygen flow

We notice the increase of rugosity of the thermally treated surface after settling down, proportional to the initial rugosity. We also notice a lower rugosity of the ZrON layer than that of TiON layer, both after settling down and the thermal treatment.

Mechanical characteristics of the settled down layers

In **table 3** we present comparatively the mechanical characteristics (microhardness, adherence) of the oxynitride layers settled down on a Ti sublayer.

Layer/Ti	**HV$_{0.010}$ (GPa)**	**L$_c$ (N)**
TiNO	**14.6**	**20**
ZrNO	**12.4**	**17**

Table 3 - Microhardness and adherence of oxynitride layers settled down on Ti sublayer

5. Conclusion

The experimental research has allowed: ▲ identification of complex Ti-based alloys destined to the attainment of osseous integration implants;▲establishing the technologic procedure for obtaining complex biocompatible materials, by applying the following technologic option:►forming of electrode by pressing (titanium sponge and alloying elements);►melting of electrode in electrical void remelting installations; ► forging of ingot on hydraulic press (successive forging to Φ100 mm bar followed by radial forging on horizontal forging machines);►intermediary thermal treatments; ►semi-warm deformation by precision radial forging-deformation from Φ40 mm to the final dimensions Φ25-Φ4 mm;►final thermal treatment and adjustment;▲ elucidation of the mechanisms of synthesis and deposition of certain bioactive compounds based on Ti oxides/oxy nitrides and/or Zr which have permitted the bio functioning for the surface of the osseous synthesis implants;▲complete characterization of the biologically active surfaces formed from compounds based on zirconium oxy nitride and/or titanium oxy nitride, produced by surface engineering techniques.

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