ASPECTS REGARDING THE EVOLUTION AND CHARACTERISTICS OF SOME TITANIUM ALLOYS USED IN ORAL IMPLANTOLOGY

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Discovered in 1791 by William Gregor and isolated from its ores in 1939 by the Kroll process, titanium was originally used as pure metal. Of all its properties, the most useful features of titanium are the corrosion resistance and the high ratio of hardness to specific weight. Non-alloy titanium is used in implantology with a purity of about 99.75% and an iron content of max. 0.5% (usually less than 0.1%). The Ti-6Al-4V alloy, commonly used for implants, has a combination of the most favorable features (very good mechanical properties and corrosion resistance) the first to produce titanium dental implants were Linkow (1968), Branemark (1969) and Hofmann (1985), which use this alloy. The need to remove some harmful chemical elements in known titanium alloys has led to the investigation of Ti-Al-Nb or Ti-Zr-Al alloys that have demonstrated (e.g. Ti-6Al-6Nb alloy) in addition to mechanical resistance and corrosion comparable to Ti-6Al-4V alloy, a decrease in the release of proinflammatory and osteolytic mediators that are responsible for the loss of prostheses. In today's modern approaches titanium-zirconium alloys are revolutionary materials whose proven characteristics are increased mechanical strength (50% higher than that of pure titanium), very good and fast osteointegration, reliability and safety, especially for low diameter implants. The paper summarizes the results of research on the characteristics of Ti-Zr alloys for oral implantology.

Keywords: evolution, characteristic titanium alloys, implantology

1. Introduction

The dental implant is a metal body that is placed in the jaw bone or mandible and which takes over the function of the dental root. Implants are defined as different devices or apparatuses of alloplastic materials which are inserted into the thickness of some dental-maxillary tissue in order to ensure the retention of a prosthetic piece. Acceptance of the implant by the body involves the formation and strengthening of the link between the implant surface and the bone tissue. P.-I. Brånemarck [1] defines the osteointegration process of the implant and

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claims that the success of the entire implantation process depends on "how close the bone grows around the implant." Having an essential role in the implant-prosthetic rehabilitation of edentations, the tissue integration of the dental implant allows for the masticatory pressures to be transmitted exactly as with the natural teeth, thus ensuring the normal comfort of mastication [1-7]. X-ray microanalysis of histological preparations from the implant-tissue interface area revealed a fully mineralized lamellar bone, with characteristic gaps and vital osteoblasts penetrating the surface of the oral implant. The bone has reached a distance of less than 0.5 μm from the surface of the metal (implant), which is considered too small for the organization of any living tissue [6,7]. The formed bone tissue attaches to the dental implant, which contributes to integrating the implant into the alveolar bone. The newly formed bone develops to the surface of the implant, and the newly formed bone trachea provides the biological fixation of the implant [8]. Though relatively narrow [8], its nature (metal oxides, protein layer, connective tissue) has a substantial role in maintaining integrity of the entire system.

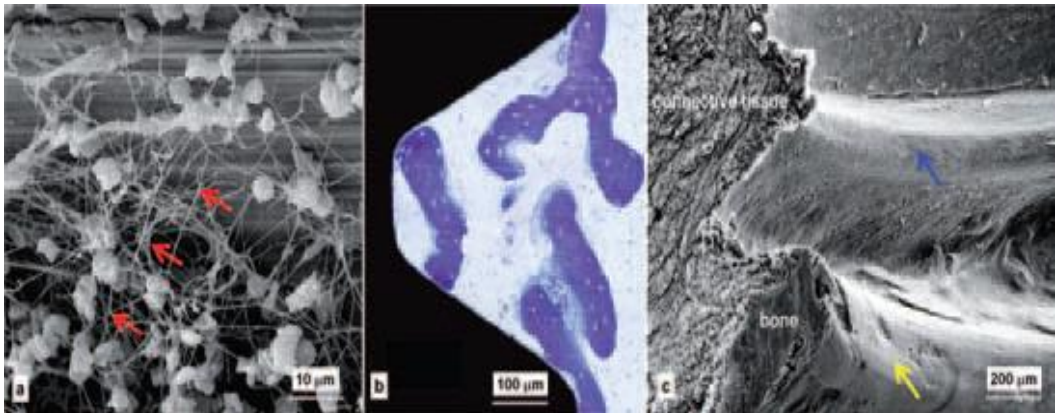


Fig. 1. Examples of understanding the implant interface in 1982: (a). fibrin (red arrows) from the peri-implant clot detached from a treated surface, (b). bone formation through remote osteogenesis, smooth interfaces between bone and connective tissue indicating the presence of tissues on the surface rather than cells in intimate interactions / surface [8, 9].

The American Academy of Implant Dentistry defines in 1986 the term osteointegration as follows: “established contact between the normal remodeling bone and the implant without interposing neosome tissue, allowing the continuous transfer of implant tasks to and into bone tissue”.

Today, in specialty studies that describe the osteointegration process, we frequently encounter the notion of biointegration of the implant, which implies the absence of the fibrous connective layer at the interface and the creation of common bone crystals between the surrounding bone and the implant surface [8, 9]. Also, in the present dental practice, rather than the notion of osteointegrated

implants, the notion of osteointegrated implants, which involves an almost direct and functional connection between a vital bone and the implant introduced into this bone, maintains tissue integration and the quality of osteoacceptance of implants, the quality of the implant biomaterial, which must be physically and biologically compatible with the alveolar bone.

The unanimous conclusion of implantology specialists is that the biomaterial must be integrated and surrounded with bone structure. Therefore, the following elements are considered in the implant - tissue analysis: implant material and tissue, implant/biomaterial effect and the nature/effect of its secondary products on local and systemic tissues and the implant - tissue interface [10]. The overall response of the body to the complex process of implantation is conditioned by factors primarily related to the material (chemical properties of volume and surface, physico-chemical stability, physical and chemical properties of degradation products), geometry and design of the implant, the host organism (tissue localization, age, gender, general health status) and the implantation method or surgical technique.

According to P.-I. Brånemark [1], at the beginning of their use, the metal implants were not integrated (osteointegrated) in the bone but tolerated by tissues, with a variable thickness of the fibrous interface that maintained the implant in the bone but without a rigid fixation. Titanium was originally used as pure metal and is considered an almost ideal material in dental endoscopic implantology, because in contact with a tissue environment it is rapidly inactivated by forming a fine layer of oxides (monoxide, dioxide, trioxide). The thin titanium oxide film (tenacious and protective) formed in less than a second provides corrosion resistance and allows the bone to develop into the implant. In fact, a strong bond is established between the titanium implant and the surrounding bone by increasing the bone on the rusty surface obtained by mechanical or chemical processing, thereby achieving a rigid, mechanical, anchilozing anchorage that stabilizes the endosomal implant. The oxide surface, consisting of TiO, TiO_3, Ti_2O_3, Ti_3O_4 attracts and binds biomolecules [11].

Titanium alloys are considered even better tolerated than pure titanium because the oxide layer being formed is thicker (about 10-20 μm), very stable and regenerates every nanosecond. The corrosion resistance of these alloys can be improved by alloying with molybdenum, zirconium, rhenium, niobium, chromium, manganese (examples such as Ti-Al-V, Ti-Al-Mo, Ti-Al-Cr-Co). The frequent choice of the Ti-6Al-4V alloy implant is based on the fact that it has a combination of the most favorable features, including high corrosion resistance, reduced elasticity and bone and other connective tissue (osteointegration) capacity. With all these advantages, however, there are a number of problems related to the effects that alloy components can have. The release of metal ions from the corrosion and wear process and the toxicity of vanadium and aluminum

ions found in tissues are associated with the cause of inflammation, being considered to be involved in osteolysis. Research in countries such as Japan, China or the USA, but also in some European countries to replace or even eliminate harmful substances, has been based on the idea that nickel and vanadium are toxic, carcinogenic, and that aluminum has a causal relationship to neurotoxicity and senile dementia of the Alzheimer's type, and the release of vanadium ions in the body, for example, can cause serious damage to the organs and blood platelet systems. There are researches that looked at the possibility of replacing vanadium with niobium by proposing alloys with a titanium base such as Ti-Al-Nb or Ti-Zr-Al. Ti-6Al-4V induces, more than other alloys, a significant increase in the release of proinflammatory and osteolytic mediators that are responsible for the loss of prostheses. The idea of replacing harmful elements in titanium-based alloys has led to the synthesis of a wide range of alloys, such as tantalum, palladium or combinations such as Nb + Ta, Nb + Ta + Pd in alloys such as Ti15Zr4Nb2Ta0.2Pd, Ti5Zr8Nb2Ta, Ti10-20Zr4-8Nb0.2Pd, a.s.o.

Along with control of chemical composition, improved cellular interaction and cell development at the interface between the organism and biomaterial [12] was proven by intensifying protein adsorption processes for titanium alloys through various implant surface processing processes. The last 15 years have been devoted to modern assessment of the modification of titanium surface microtropography for dental implants in order to determine if bone prosthesis could be strengthened by a microrugous surface obtained by various processing techniques such as sandblasting, acid attack, or their combinations [13]. The use of the combination of the titanium properties as biotolerated material and the properties conferred by the bioactive film have directed research into the deposition processes known today as follows: Plasma Spray, Flame Spray at 3000°C (High viscosity flame spray), glazing, Pulsed Laser Deposition, Pulsed Electron Deposition, Magneto-Sputtering Deposition, Electrophoretic Deposition, Chemical Vapor Deposition, Physical Vapor Deposition, HA Blast Coating, Soil Gel Deposition, Melt Immersion, Chemical Deposition of Biological HA from Blood Solution-Related Solutions on H_2O_2-Activated Surfaces, or Basis, Chemical Deposition Biological HA from Blood Plasma - like Solutions [9].

With comparable resistance to the implant obtained by conventional techniques, the titanium implant obtained by LST-Lase Sintered Titanium, launched in 2009, has a rusty microporous surface of 2-200 μm and a geometry that allows control of the interface properties tissue - implant. The Trabecular Metal Implant [14, 15], the latest breakthrough in the field of dental implantology, the only three-dimensional (3D) implant (Fig. 2) imitating bone cell architecture (80% porosity) and the systematic nanotuberature topography of superficial areas.

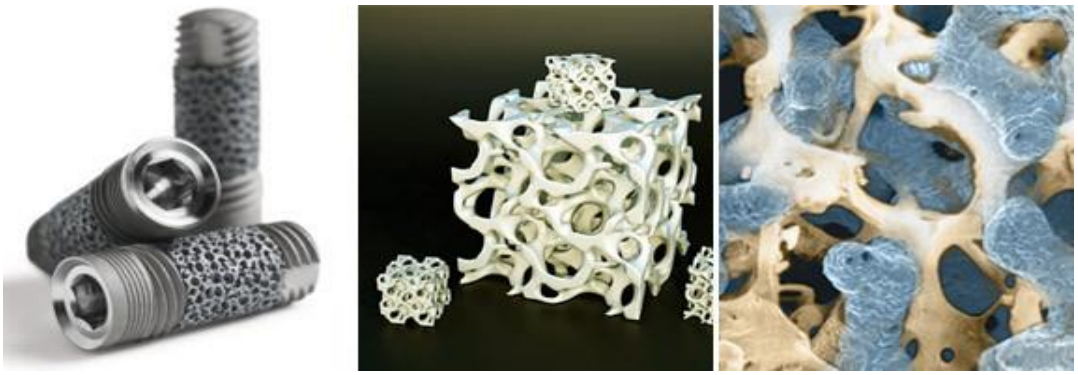


Fig.2. Trabecular metal implant that imitates bone architecture [14]

Modern design has revolutionized conceptually the theory of osteointegration, introducing the notion of osteoincorporation (the growth of bone tissue including the implant structure). The material from which the implant is manufactured is tantalum, biocompatible metal like titanium or zirconium, but which has a major advantage, namely that of natural elasticity, just like the human bone. The Roxolid implant, the latest generation and the spearhead of the producing house (Straumann), patented in 2009, is a material made up of 85% titanium and 15% zirconium for dental implants of all sizes. Roxolid is a revolutionary material specifically designed for dental implantology, its most important features are increased mechanical strength (50% higher than pure titanium), very good and fast osteointegration, reliability and safety, especially in the case of implants with a reduced diameter. It is believed that titanium-zirconium alloy has a higher biocompatibility than pure titanium [15]. This combination of properties, namely high mechanical strength and osteoconductivity (driving growth and bone regeneration) is considered unique in the dental implant market. The implants have a chemically modified and moderately rugged SLA (Sandblasting with Large Grit followed by Acid etching), which increases the bone-implant contact surface. Active SLA is the only surface texture with osteoinductive effect in the world (Fig. 3). The innovative solution for the Roxolid implant brings the following benefits: elimination of the bone addition procedure, osteointegration and rapid healing, compatibility with a large range of prostheses, octopus and dental crowns for results as close as possible to a natural tooth, both a esthetically and functionally, strong and precise bond between abutments and implants, high stability, guaranteed by the cylindrical outer contour that tracks the optimal tissue response and allows for an extended bone link.

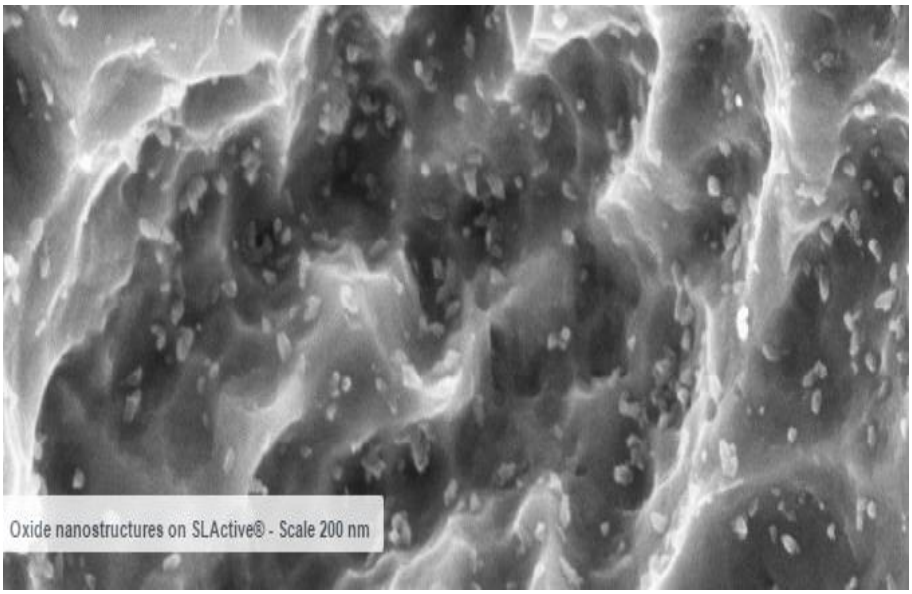


Fig.3. Nanostructured oxide on the active SLA surface [15]

In the paper are presented some research results that aimed at the behavior of a new non-harmful Ti10Zr alloy that has demonstrated high corrosion resistance in simulated medium [16,17], high biocompatibility in vitro studies by evaluating cytotoxicity, cell adhesion and spread as well as appropriate mechanical properties.

2. Experimental procedure

The studied alloy has an original chemical composition consisting of 90% Ti and 10% Zr, determined on the basis of preserving the characteristics of excellence that pure titanium (good corrosion resistance, low specific gravity, low modulus of elasticity) and improvement, by zirconium (10%) intake of fatigue resistance in strongly corrosive environments such as biological fluids (Table 1).

Considering the purpose of the alloy, has been rigorously respected the quality of purity of the raw materials used that influences the content of the impurities in the final alloy, including those of the gaseous (nitrogen, hydrogen), which are strictly limited.

Table 1

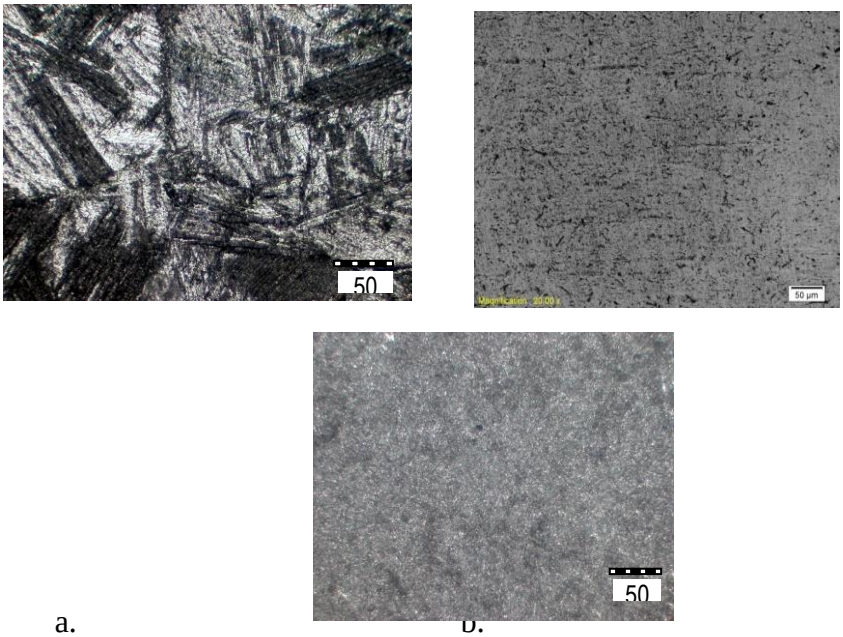
Chemical Composition and Mechanical Properties of the Ti10Zr Alloy [9]

Chemical composition, %						
Elements	Ti	Zr	Fe	Si	Cu	Ni
[%]	88,8	9,906	0,608	0,392	0,032	0,010

The resulting final products are cylinders with a diameter of about 18 mm and a length of about 70 mm. These semi-finished products have been processed until the end product is obtained, i.e. self-tapping screw self-tapping implant (Fig. 4, Fig. 5). Appraisal of mechanical properties values is one of the main steps in the characterization of a biomaterial under certain stress conditions. From the molded preform were made the standard specimens which were subjected to mechanical tests on the universal machine for the static axial traction test (Fig. 6).

Fig.4. Technological steps for obtaining of the self-tapping screw dental implant [9]

3. Experimental Results / Characterization of the $Ti_{10}Zr$ alloy



a. b. c.

Fig.5. Microstructural aspects (optical microscopy) of Ti10Zr alloy, samples with diameter ø18mm in the state: **(a).** molding; **(b).** casting + heat treatment (homogenizing annealing); **(c).** cold rolled to 3mm diameter [9]**.**

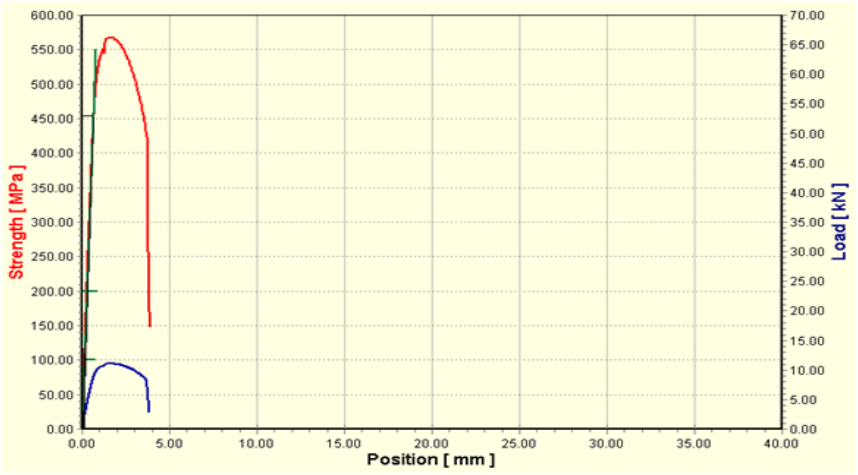


Fig.6. Traction static test diagram

Table 2

Physico-mechanical properties of the Ti10Zr alloy

Available	Shortname	Value	Unit	Tolerance	Minimum	Maximum
Tensile srenght	U.T.S.	576,86	MPa	ok	-10000,00	10000,00
Load max	Fm	11,04	kN	<	100,00	200,00
Elongation	A	19,73	%	ok	-10000,00	10000,00
E-modulus	Emod	73,34	GPa	ok	-10000,00	10000,00
Position at Fmax	WegFmax	1,53	mm	ok	-10000,00	10000,00
Position at falue	WegB1	3,85	mm	ok	-10000,00	10000,00
Yield point ReH	ReH	0,00	MPa	ok	-10000,00	10000,00
Yield point ReL	ReL	0,00	MPa	ok	-10000,00	10000,00
Deformation limit Rt1	Rt1	109,25	MPa	ok	-10000,00	10000,00
Rp at D2	Y.S.	454,04	MPa	ok	-10000,00	10000,00

Table 3

The influence of degree of deformation on the hardness of Ti10Zr bioalloy [9,18,19]

No.	Samples with the diameter Φ	Partial deformation degree $C=S_{i-1}/S_i$	Total deformation degree $C_T=S_0/S_i$	Hardness HV_{100} daN/mm^2
1	Cast Φ18	0	0	212
2	Extruded Φ10	3,24	3,24	290
3	Extruded Φ5	4	12,96	306
4	Laminated Φ3	2,77	36	320

Surface fracture study by electron microscopy analysis at different magnifications highlights the rupture (test-to-traction test specimen) defined as

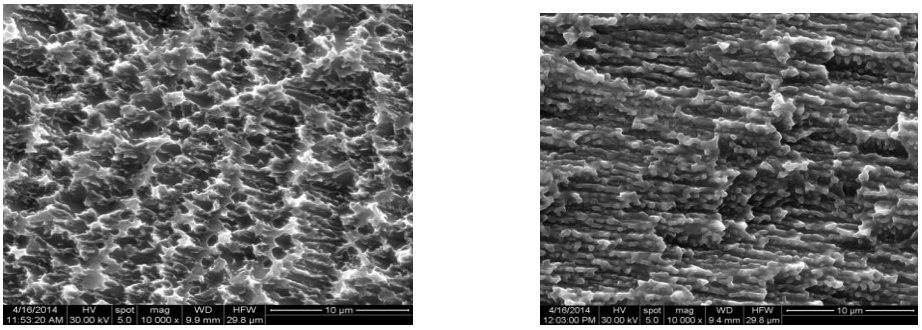
ductile fracture, which confirms the good behavior of the alloy in deformation hot and cold plastic [18].

The deformation processing ensures a fine structure and an increase of about 50% of the hardness and strength properties [19,20].

Ti10Zr alloy samples were processed superficially by chemical and electrochemical methods (acid corrosion, anodic oxidation) to activate the tissue-metal / implant interaction. Scanning electron microscopy analysis [21-26] of experimentally processed samples showed that their surface was covered with a uniform, continuous and adherent titanium oxide layer (Fig.7 a, b).

In vitro biocompatibility bioalloy testing provided information on the cytotoxicity and cellular behavior [27-30]. Cytotoxicity was determined by exposing G292 osteoblasts and assessing the level of LDH released in the extracellular medium as a measure of the degree of inhibition of cell growth caused by the test material. The cytotoxicity caused by the exposure of osteoblasts to Ti10Zr alloy was evaluated by quantifying plaque membrane damage.

The level of LDH released in the extracellular medium is a measure of the degree of inhibition of cell growth caused by the test material. After examining the actin filament architecture at the fluorescence microscope after 24 and 48 hours of Ti10Zr cultivation it was observed that the cells grown in the monolayer and showed an osteoblast-like phenotype, with no major differences in the organization F-actin between these cells and those control. Also, isolated round cells representing osteoblasts in the division were noted [30].



a. **b.**

Fig.7. Microscopic aspects (SEM) of corroded sample morphology **(a)** and anodized / anodic oxidation **(**b) [22, 26]

Good adhesion of osteoblasts has been demonstrated on these surfaces, with cells displaying a well-organized actin cytoskeleton with cytoplasmic extensions interconnecting neighboring cells, which are arranged at cell densities comparable to those of control. Regarding the F-actin structure in the adherent cells on the surface of the test materials, it was observed that the osteoblasts adhered to a much smaller number on these surfaces, being spaced apart from

each other. The glutathione level in the cells can define their proliferative capacity as the principal thiol non-proteolytic antioxidant that is involved in the regulation of sensitive redox proteins. Fluorescence labeling of GSH by CMFDA revealed an almost similar distribution of this molecule in cells cultured on Ti10Zr surfaces compared to control sample. Quantification of GSH-CMF fluorescence in cells adhered to the Ti10Zr material showed that the GSH and cytoplasmic levels were similar to control sample (approximately 100%) after 24 hours, increasing by 12% and 17%, respectively, after another 24 hours. This increased level proves that the surface of the material stimulates cell proliferation after 48 hours of cultivation due to intrinsic properties that provide the conditions for good cell growth. Thus, Ti10Zr biocompatibility is demonstrated by all tests performed in this in vitro study which demonstrate the efficacy of the material to induce human osteoblast adhesion and cell proliferation. Its proven biological properties (lack of cytotoxicity) recommend it as a biomaterial for the manufacture of medical devices, such as dental implants [9, 30].

4. Conclusions

The paper presents a synthesis on the compositional characteristics of titanium alloys used in oral implantology, the necessity and the steps taken to eliminate the toxic elements for the body and research on a new high biocompatibility alloy (Ti10Zr), controlled by the chemical composition. Some of the results of the research on the mechanical and biological behavior of the Ti10Zr alloy that demonstrates the alloy's ability to be successfully used for oral implants are also presented.

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