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BIOLOGICAL BEHAVIOR AND CORROSION OF PROSTHETIC AND ORTHODONTIC TITANIUM IMPLANTS

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ABSTRACT

Titanium and its alloys are used in dentistry for implants because of their unique combination of chemical, physical, and biological properties. For dental implants, biocompatibility depends on mechanical and corrosion/degradation properties of the material, tissue, and host factors. Corrosion can severely limit the fatigue life and ultimate strength of the material leading to mechanical failure of the dental materials. Titanium and its alloys provide strength, rigidity, and ductility similar to those of other dental alloys. Whereas, pure titanium castings have mechanical properties similar to Type III and Type IV gold alloys, some titanium alloy castings, such as Ti-6Al-4V and Ti-15V have properties closer to Ni-Cr and Co-Cr castings with the exception of lower modulus.

This article presents a few considerations and results of studies regarding the biological behavior and corrosion resistance of the commercially pure titanium (CP Ti), titanium alloys (e.g. Ti6Al4V) by comparation with other alloys (stainless steel orthodontic mini implants for example, fig.) used in prosthetic or orthodontic implant technology. The goal of the study is to determinate the main parameters (factors) and the way they affect (integrity, stability) the utilisation performance of the stainless steel orthodontic mini implants.

KEYWORDS: miniimplant, orthodontic anchorage, biocompatible metallic material, titanium, stainless steel

1. Introduction

Biocompatibility would be perfect without any biomaterial- tissue interactions and could be ensured by a completely inert biomaterial, which does not exist at this time.

Human body's internal environment is aqueos with a pH of 7,4 and a temperature of 37^{0}C; the aggresive saline content is an excellent electrolyte to facilitate hydrolysis and electrochemical reactions of corrosion and the existance of cell capacity which will certains be catalyzed by chemical reactions and will destroy the various species identified by the body as foreign. Biomaterials degradation occurs by corrosion (conventional) passive and active corrosive in particular, by the presence of cellular and molecular species.

For this reason, the precious metallic biomaterials and their alloys are used (less often because they are expensive) but also the common metals and metal alloys such as: Ti, Ti–Al–V, Ti–Ni, Ti–Al, Fe, Ti–Al–Nb, Co–Cr–Mo, Co–Ni–Cr–Mo, Co–Cr–W–Ni, stainless steel with 18%Cr and 8%Ni.

Table 1. *Chemical composition of unalloyed titanium as biomaterial*

Element	Compositional limit, [%]			
	Grade1 max	Grade 2 max	Grade 3 max	Grade 4 max
Nitrogen	0.03	0.03	0.05	0.05
Carbon	0.1	0.1	0.1	0.1
Hydrogen	0.0125	0.0125	9.0125	0.0125
Iron	0.15	0.2	0.25	0.3
Oxygen	0.18	0.25	0.35	0.45
Titanium	Balance	Balance	Balance	Balance

Titanium is an inert material which has the objective to be a medium in contact with tissue and is inactivated rapidly by forming a thin layer of tough and protective oxide. Surface oxide consists of TiO, TiO_3, Ti_2O_3, Ti_3O_4, and it retains and binds biomolecules. Contaminated surface changes the composition of oxide, favoring inflammation which is followed by formation of granulation tissue.

Table 2. *Mechanical properties of unalloyed titanium as biomaterial*

Grade	**Conditions**	**Tensile strength** min, MPa	**Yielding strength** min, MPa	**Elongation** min, %	**Reduction of area** min. %
1	annealed	240	170	24	30
2	annealed	345	230	20	30
3	annealed	450	300	18	30
4A	annealed	550	440	15	25
4B	cold worked	680	520	10	18

Titanium implants are often covered throught the TPFS (Flame Titanium Plasma Spray), by hydroxyapatite or zirconia layers which give them a better osteointegration.

Table 3. *Chemical composition of titanium based alloys as implants for surgery*

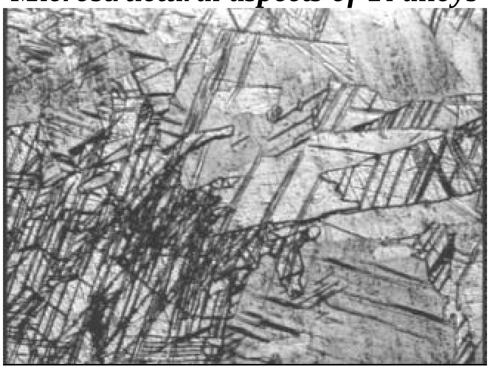
Element	**Ti6Al4V Wrought**	**Ti5Al2,5V Wrought**	**Ti6Al7Nb Wrought**
Aluminium	5.5-6.75	4.5-5.5	5.5-6.5
Vanadium	3.5-4.5	-	max.0.5 tantalum
Iron	max.0.3	2-3	max.0.25
Niobium	-	-	6.5-7.5
Oxygen	max.0.2	max.0.2	max.0.2
Carbon	max.0.08	max.0.08	max.0.8
Nitrogen	max.0.05	max.0.05	max.0.05
Hydrogen	max.0.015	max.0.015	max.0.009
Titanium	balance	balance	balance

Table 4. *Mechanical properties of titanium based alloys as implants for surgery*

Alloys	**Tensile Strength** min, MPa	**Yielding Strength** min, MPa	**Elongation** min,%
Ti-6Al-4V wrought	860	780	8
Ti-5Al-2.5V wrought	900	800	8
Ti-6Al-7Nb wrought	900	800	10

Advantages of titanium are shown not only in implants made of it, cones, hand tools and compmnents (which are obtained by cold deformation), but also in different pluridentare fixed partial denture made by casting. Another thing that has been specially designed consist of titanium ceramic bodies. Areas of use of titanium in dentistry and oro- maxilofacial surgery are constantly expanding.

Microstructural aspects of Ti alloys



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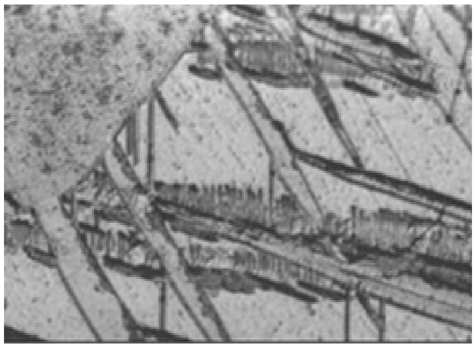

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Table 5. *Comparison of metallic biomaterials [21]*

Alloy properties	**AISI 316L**	**CoCr cast**	**CoNiCr wrought**	**Ti-6Al-4V**	**Cp Ti**
Corrosion	-	-	+	+	+
Biocompatibility	-	-	-	+	+
Bioadhesion	-	-	-	+	+
Biofunctionality	1.2	1.5	2.3	5.2	1.8
Processability	C D W P	C W P	C D W P	C D W P	C D W P
Casts (DM/Kg) Semifinished product	-60	-60	-70	-75	-70

C-casting; D-deformation; W-Welding; P-powder metallurgy

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2. Studies and research on corrosion resistance of metallic biomaterials

Long-term studies on electrochemical behavior of some alloys based on Co-Cr, Ni-Cr, Pd şi Ti in artificial saliva show that titanium has the lowest rate of release of ions followed by alloy Co-Cr, Ni-Cr with more than 20% Cr, Ni-Cr, with less than 20% Cr and Pd alloys. The corrosion resistance of titanium dental purpose is influenced by several factors, which include: type of technolgy used to obtain finished parts, processing handled, finishing and polishing action as well as the action of the cleaning agents and solvents.

Corrosion tests conducted in artificial saliva showed that the penetration potential of titanium is much higher than other dental alloys, thereby justifying its resistance to corrosion (Table 6).

Table 6. *Penetration potential of alloys titanium*

Dentistry alloy/titanium	Penetration potential (mV)
Gaudent S	-100
Au – Ag – Pt	+780
Ni – Cr – Mo	+820
Co – Cr – Mo	+920
Ti unalloyed	> 2000
Dentistry alloy/titanium	Penetration potential (mV)
Gaudent S	-100
Au – Ag – Pt	+780
Ni – Cr – Mo	+820
Co – Cr – Mo	+920
Ti unalloyed	> 2000

Titanium alloys seem to be better tolerated than pure titanium as oxide layer whose form is 10-20 µm. Recent research has shown that the layer of TiO considered so stable regenerates every nanosecond. Traditional corrosion test consists in the measurement of weight change in specimen during exposure to a corrosive environment.

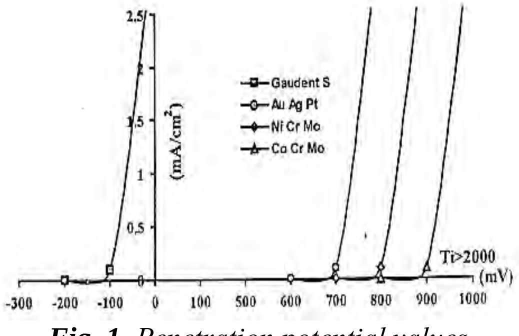

Fig. 1. *Penetration potential values corresponding to some dental alloys and titanium.*

The main disadvantage of weight loss measurement is the inability of the method to predict the corrosion rate if the exposure of the alloy to the corrosive environment is significantly extended more than the experimental exposure. Other testing methods of the implantable metallic materials are based on the use of optical microscopy, X-Ray spectrograph, the spectrochemical analysis and electronic probe microanalysis. While these methods can provide valuable information about the corrosion products, they are tainted by the transport of the products to more dispersed tissues in the body and by the excretion of corrosion products in urine, sweat and faeces. Electrochemical methods have been widely used for estimating corrosion in surgical alloys. The most important methods are electrochemical anodic back EMF, time-potential test, polarization curves and polarization resistance technique.

Considering a specific electrolyte that simulates body fluid, respectively Hank's solution, the current density of different biomaterials as a function of the potential difference between the anodic and cathodic branches of the current potential curves is shown in Figure 2.

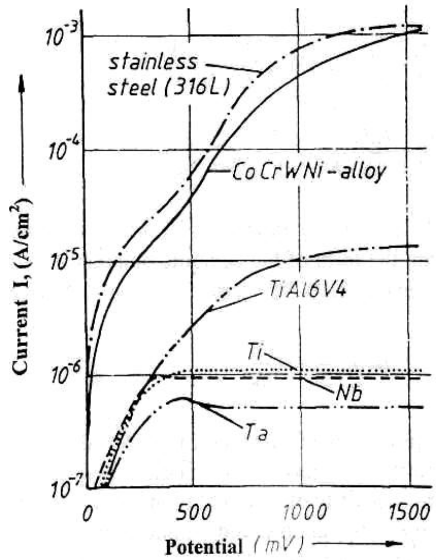

Fig.2. *Current density as a function of the potential difference between the anodic and cathodic branches of the current – potential curves for metals tested in 0.9% NaCl with a stable redox system [Fe $(CN)_6^{4-}$/F$(CN)_6^{3-}$] /21/*

The saline containing this redox system [0,9% NaCl in $Fe(CN)_6^{-4}/F(CN)_6^{3-}$] resembled closely in its resting potential that is a tissue culture fluid, which has its redox potential at 400mV. As it can be seen titanium and titanium alloys, tantalum and niobium behave in a more noble way than the stainless steel AISI 316 and a wrought CoNiCr-alloy.

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Considering the same Hank's solution (0.17M NaCl; 22^{o}C) the comparative potential/time curve of scratch tests of implant alloy is given in Figure 3.

As it is illustrated in Figure 3 for a metal such as titanium, which is resistant to crevice attack, repassivation occurs within a few seconds.

The potential time transient shows an initial drop in potential at the time of scratch with rapid rise in potential to the prescratch „passive" value.

For alloys, such as 18Cr-10Ni (AISI 316L), an austenitic stainless steel, which requires an oxygen cathode, a different potential curve is recorded.

At the time of the scratch, a potential drops to a value consistent with the active dissolution of the scratch. It never returns to its potential value, since repassivation cannot occur.

Table 7. *Corrosion rates of biomaterials in Hank's solution*

Alloy	**Metal converted into compound,** ng/m^{2}h	**Metal found in tissue**, ng/m^{2}h
Stainless steel – mechanically polished (AISI 316L) – chemically polished	7.8 230	0.274 -
Vitallium – mechanically polished (CoCrW-Ni alloy) – chemically polished	150 20	0.249 -
Ti – mechanically polished – chemically polished	4.1 3.5	0.430 -

Considering another criterion of corrosion resistance, as formation of corrosion products, in Table 7 it is given a comparison of rate of corrosion product formation for biomaterials in Hank's solution during current-time tests with rate of formation of implant corrosion products in rabbits.

So the values in Table 6 represent dissolution rates for titanium alloys several orders of magnitude less rapid than those measured for passive stainless steel alloys.

The same behavior can be observed during the measurements of the polarization resistance of different metallic biomaterials (as given in Table 8).

Breakdown potential measurements of different implant materials in Hank's solution resulted also in a clear order of ranking of the different materials. While commercially pure titanium and TiAl6V4 had high breakdown potentials of 2.4 and 2.0 V respectively or stainless steels and CoCr alloys (cast an wrought) this value amounted only to 0.2 and 0.42V respectively, as given in Table 9.

So, titanium and its alloys, niobium and its alloys and tantalum belong to the group of metals, which in body fluids cannot undergo a breakdown of passivity. In this fluid, a breakdown at a high potential causing a pitting corrosion is impossible because it is more positive than the oxygen reversible reduction and it is less positive than the water or hydrogen- ion reduction.

In all materials the passive layer can be damaged mechanically, e.g. by fretting metal on metal (plate/screw) or by the instruments used during surgery. The time of the repassivation of the material is therefore very important.

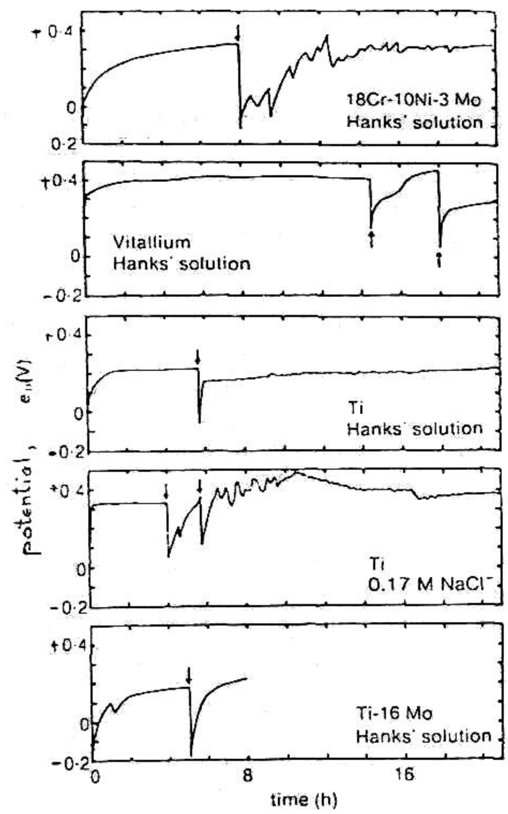

Fig.3. *Schematic diagram to show potential/time curves of scratches test of implant alloys in Hank's solution and 0,17 M NaCl solution at 22°C specimen scratched 22^{o}C ↓ specimen scratched /21/.*

The repassivation behavior of different materials in saline solution was measured using an electrode, which rotates by $10s^{-1}$ in saline solution whereby it is activated by a cutting tool of Al_2O_3. The decrease of the corrosion current is measured in dependence on the time at different potentials. The repassivation is defined to be achieved, if the current density amounts to 1/e (e≈2,718) of the current density in the achieved condition. In addition, the time $t_{0,05}$ of a rest active current density 5% was determined. The values t_e and $t_{0,05}$ of the different measured materials are also given in table 8.

The passive oxygen surface layer (t_e) is reconstructed dependent on the material in some milliseconds. The growth of the surface layer ($t_{0,05}$) of titanium and titanium alloys is accelerated compared to the other materials.

Table 8. *Polarization resistance of metallic biomaterials in 0,9 NaCl with stable redox system [Fe $(CN)_6^{4-}$/F$(CN)_6^{3-}$] /21/*

Metallic biomaterial	**Polarization resistance** [kΩcm^2]
Au	0.28
FeCrNiMo (AISI 316L)	4.38
Co NiCr (wrought)	3.32
Ti	714
TiAl6V4	455
Nb	455
Ta	1430

Table 9. *Breakdown potential in Hank's solution of metallic biomaterials and repassivation time 0,9% NaCl [21]*

Metallic biomaterial	**Breakdown potenţial** (V)	**Repassivation time** (msec)			
		t_c		$t_{0,05}$	
		(s)	(s)	(s)	(s)
AISI 316	+0.2-0.3	>72000	35	>>7200	>6000
CoCr	+0.42	44.4	46	>>6000	>6000
CoCrNi	+0.42	35.5	41	>6000	5300
TiAl6V4	+2.0	37	41	43.3	45.8
Ti	+2.4	43	44.4	47.4	49
Ta	+2.25	-	-	-	-
Nb	-	47.6	43.1	47	85

3. Experimental Conditions

This article draws attention to current concerns of a research team composed of chemists, metallurgists, dentists about stainless steel mini implants for orthodontic anchorage characterization from the chemical and biological point of view compared to the usual metal alloys which are used nowadays in the manufacture. A painstaking ongoing research program aims at the use of advanced investigation methods such as: optical and electronic microscopy, study of corrosion resistance and surface microtopography also keeping the comparison with titanium and its very studied alloys and in many cases with controversial views. Anchorage has long been a challenge since the introduction of fixed appliances in orthodontics [3]. Typically, orthodontic movement of a tooth is anchored by a large group of teeth so as to minimize undesired displacements of anchoring teeth. Adequate anchorage becomes difficult when posterior teeth are missing. Intra- and extra-oral auxiliary devices can be used to assist movement, but the effectiveness of these measures is dependent upon the level of the patient's cooperation [3].

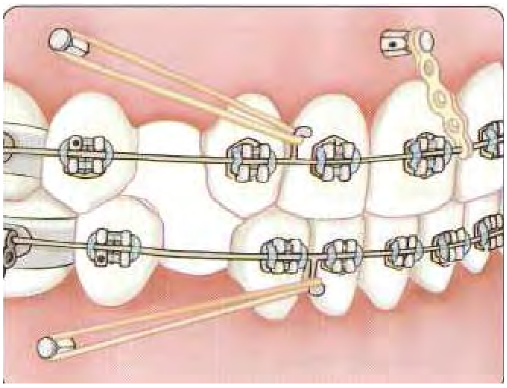

Fig.4. *Insertion procedure of orthodontic mini implants [22].*

Conventional titanium implants have emerged as an excellent alternative to traditional orthodontic anchorage methodologies, mainly when anchorage dental elements are insufficient in quantity or quality. Unfortunately, conventional dental implants can only be placed in limited sites, such as the retromolar and edentulous areas. In addition, conventional dental implants are troublesome for patients because of the severity of the surgery, the discomfort of the initial healing and the difficulty of maintaining oral hygiene.

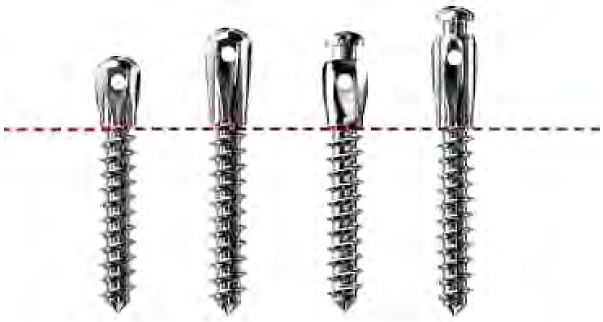

Fig. 5. *Stainless steel orthodontic mini implants [22].*

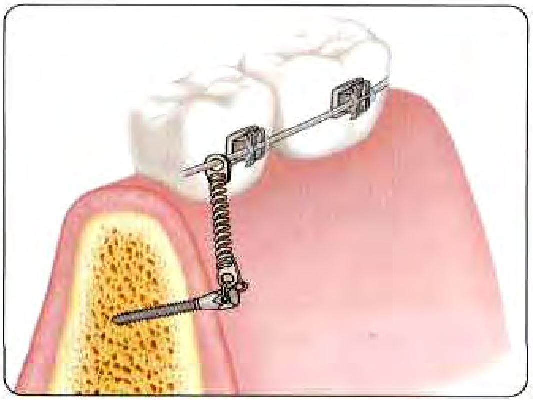

Fig. 6. *Connection of the mini implant to the orthodontic appliances[22].*

Due to these disadvantages, Kanomi proposed titanium mini-implants (1.2 mm in diameter and 6.0 mm in length) for orthodontic anchorage.

They are widely used since they have few implantation site limitations, a simple insertion procedure and easy mechanical force control.

The methodology for implementation of mini-implants has been continuously improved. Some complications persist, and the sources of failure include the inflammation of the soft tissue around the mini-implant and fracture of the mini-implant [3].

A period of healing is usually necessary before applying load to conventional dental implants. This period varies from 4 to 6 months in humans [3]. When the load is placed prematurely, histological analyses have suggested that there is no uniform intimate bone-implant contact due to interplayed fibrous tissue. This phenomenon could be favorable for implants for orthodontic anchorage purposes, since it facilitates the surgical removal of the implant at the end of the orthodontic treatment. On the other hand, the excess of interplayed fibrous tissue could lead to implant failure.

Commercially pure titanium (CP Ti) is widely used as implant material because of its suitable mechanical properties and excellent biocompatibility.

However, CP Ti has lower fatigue strength than titanium alloys. Ti–6Al–4V can be used to overcome this disadvantage [3]. However, the corrosion resistance of the mini-implant decreases when the alloy is used, favoring metal ion release, which has been associated with clinical implant failure, osteolysis, cutaneous allergic reactions, remote site accumulation, kidney lesion, cytotoxicity, hypersensitivity and carci-nogenesis [3].

Fig. 7. *Orthodontic stainless steel mini implants studied.*

Fig.8. *Hexagonally shaped head.*

Orthodontic stainless steel mini implants studied are designed for temporary insertion and can be loaded with tractions (springs, wire, elastics, chains), to get dental movements with the biomechanical advantage of the maximum anchorage and in critical anchorage situations due to the lack of teeth (periodontal involved or edentulous patients).

Following some possible applications are indicated: inter-arch extrusion, intra-arch intrusion on anterior teeth, intra-arch intrusion on posterior teeth, surgical disinclusions (cuspids, etc.), orthodontic anchorage for distalization, orthodontic anchorage (i.e. after distalisation).

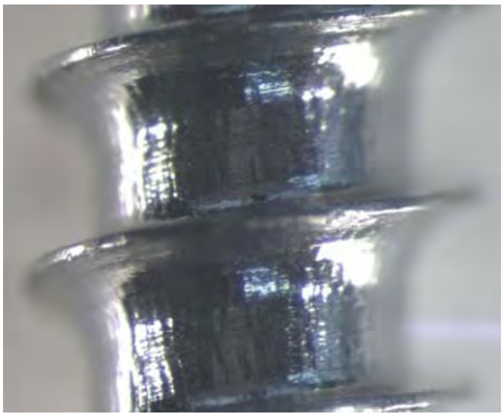

Fig.9. *Cylindrical screw design.*

Fig. 10. *Machined surface.*

Traction devices are tied through the passing hole present on the head of the mini implant or anchorage at the groove featured by some models:

- with low head (transmucosal height of 1.75 mm)
- wich high head (transmucosal height of 3 mm), and two different versions.

The first one with a passing hole on its head, while the second one presents a groove in addition to the hole. The groove- added version has the prominent part similar to an orthodontic button to facilitate the application of chains, elastics or springs.

The application time of the orthodontic traction on the mini implant depends on the clinician's judgement; the mini implant can usually be loaded immediately after insertion or after healing of soft tissues. They can be easily removed after use by simply unscrewing them in the opposite direction.

4. Conclusions

This paper has presented a short summary of the characteristics of metallic biocompatible materials for dental implants, mainly of titanium and titanium alloys, in particular highlighting the corrosion behavior in environments simulating oral environment and by comparison with other alloys, for example stainless steels.

A major research program has begun aiming at the chemical and physico-mechanical characteristics determination but also at characterizing the behavior in oral environment of stainless steel anchorage mini implants. Ongoing investigations are made by modern techniques and equipment performance (SEM, EDX, AFM, after corrosion and tribocorrosion tests etc) samples of materials known but alternative materials.

References

[1]. Nicolas Schi, Brigitte Grosgogeat, Michele Lissac, Francis Dalard, Biomaterials 23 (2002) 1995-2002.

[2]. M.A. Khan, R.L. Williams and D.F. Williams, *Biomaterials* 17 (1996) 2117-2126 © 1996 Elsevier.

[3]. Liliane S. Morais, Glaucio G. Serra, Carlos A. Muller, Leonardo R. Andrade, Elisabete F.A. Palermo, Carlos N. Elias, Marc Meyers, Acta Biomaterialia 3 (2007) 331-339

[4]. H.J. Rack, J.I. Qazi 1, Materials Science and Engineering C 26 (2006) 1269 - 12775.

[5]. M. Karthega, V. Raman, N. Rajendran, Acta Biomaterialia 3 (2007) 1019-1023

[6]. Zhuo Cai, Ty Shafer, Ikuya Watanabe, Martha E. Nunn, Toru, Okabe, Biomaterials 24 (2003) 213-218

[7]. Sergio Luiz de Assis, Stephan Wolynec, Isolda Costa, Electrochimica Acta51 (2006) 1815-1819

[8]. D.D. Deligianni, N Katsala, S. Ladas, D. Sotiropoulos, J. Amedee, Y. F. Missirilis, Biomaterials 22 (2001)1241-1251

[9]. J.Ge and O.B. Isgor, Materials and Corrosion 2007, 58, No. 8, pg. 573, 583, 616

[10]. Hesham E. Khalifa, Kenneth S. Vecchio, Advanced Engineering Materials No. 11/2009

[11]. M.F.Lopez; A. Gutierrez; J.A. Jimenez, Surface Science 482-485

[12]. C. Morant, M.F. Lopez, A. Gutierez, J.A. Jimenez, Applied Surface Science 220 (2003) 79-87

[13]. E. Eisenbarth, D. Velten, M. Muller, R. Thull, J. Breme, Biomaterials 25 (2004) 5705-5713

[14]. Mitsuo Niinomi, Journal of the Mechanical Behavior of Biomedical Materials 1 (2008) 30-42

[15]. S. Sathish, M. Geetha, N.D. Pandey, C. Richard, R. Asokamani, Materials Science and Engineering C 30 (2010) 376-382

[16]. Ramakrishna Venugopalan, Michael A. George, Jeffrey J. Weimer, Linda C. Lucas, Biomaterials 20(1999) 1709-1716

[17]. Yu Zhentao, Zhou Lian, Materials Science and Engineering A 438-440 (2006)391-394

[18]. Robert G. Craig Restorative Dental Materials, 1997 Mosby year Book, Inc.

[19]. William R. Proffit, D. D.S ; PH.D Henry W. Fields, Jr., M.S., M.S.D.; and James L. Ackerman, Peter M. Sinclair, Paul M. Thomas, J.F. Camilla Tulloch, Second Edition Contemporary Orthodontics, Mosby Year Book, 1992

[20]. Kenneth J. Anusavice, D. M. D., Ph. D. Tenth Edition Phillips' Science of Dental Materials, 1996

[21]. B. Ghiban, Metallic Biomaterials, Editura Printech 1999

[22].* Orthodontic Mini implants, Leone Clinical procedure for positioning.