THE ANNALS OF "DUNAREA DE JOS" UNIVERSITY OF GALATI.
FASCICLE IX. METALLURGY AND MATERIALS SCIENCE
N^0. 2 – 2013, ISSN 1453 – 083X

CHARACTERIZATION OF THE DENTAL METALS AND ALLOYS

*Elisabeta VASILESCU[1], Vlad-Gabriel VASILESCU[2]
Alexandru Mircea NICOLAU[2]
[1]"Dunărea de Jos" University of Galati, Faculty of Materials and Environment Engineering,
47, Domnească Street, RO-800008, Galati, Romania
[2]"Carol Davila" University of Bucuresti, Faculty of Dentistry Medicine,
Dionisie Lupu Street, 37, Bucuresti, Romania
*Corresponding author
email: elisabeta.vasilescu@ugal.ro

ABSTRACT

Metals and alloys in dentistry have seen remarkable progress due to their biocompatibility and deepen research on the application of advanced technologies to improve surface properties by controlling interactions material - environment in the mouth. Biocompatibility of metals is a consequence of the presence of surface oxide layer. Chemical properties and therefore chemical processes determine precisely this interface oxide layer and not the metal itself. Biocompatibility would be perfect without any biomaterial - tissue interactions and could be assured by a completely inert biomaterial, which does not exist at this time. 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. Co-Cr alloys are alloys nenobile group, developed as an alternative to noble alloys, which have become very expensive, inaccessible and limited resources. Modern alloys based on Co-Cr, due to its superior mechanical and cost-effective price noble alloys have replaced the classic class IV in technology (metal-polymer) and modern (metal and metal-ceramic composite). Co-Cr alloys have advantages related to high modulus (250GPa) than type IV gold alloys (70-100GPa) but they maintain their rigidity, which means that all items may have minimum thickness metal frame.

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), in comparison with other alloys (stainless steel, Co-Cr alloys) used in prosthetic or orthodontic implant technology.

KEYWORDS: biocompatible metallic material, corrosion resistance, biological behavior, titanium and titanium alloys, stainless steel, cobalt- chromium alloys

1. Introduction

Metallic biomaterials represent an important class of materials for dentistry due mainly to their mechanical properties and an acceptable biocompatibility. The biocompatibility of dental materials depends on their composition and on the location and interaction of the oral cavity.

Material response to changes in pH, the application of force or the degradative effects of fluids may affect bio-compatibility. The main issues to be considered when using metallic materials as biomaterials in dentistry (dentures, implants) include: the corrosion, release of toxic metal ions, attrition and lack of elasticity. Toxicity of metal ions as particles resulting from wear are the main disadvantages of using metallic materials as biomaterials, as they can induce multiple tissue reactions, including osteolysis, degradation of the normal bone structure, severe reaction of macrophages, granulomas, fibrous capsule, inflammatory and immune reactions. All this can lead to destabilization and weakening of prostheses and implants. In general, corrosive metals determine an acute toxic reaction.

2. Comparative study of the corrosion resistance and biocompatibility of dental metals and alloys (titanium, titanium alloy, stainless steel, cobalt-based alloys)

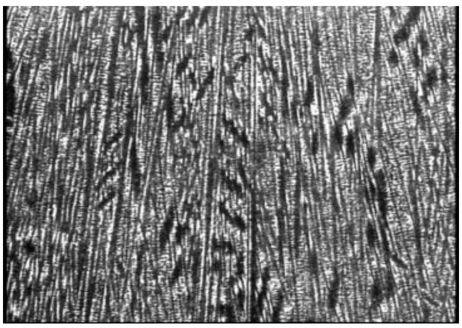
A study on the resistance to corrosion of biomaterials for implants [10], expressed by the rate of corrosion and the rate of formation of corrosion products in Hank's solution resulted in the following data (table 1) [10, p.67]. Among metals for medical applications, the best biocompatible titanium has the highest potential scale ABE-Anodic Back Electromotive Force determined in blood serum at 37^{0}C [8] and is well tolerated by living cells without place changes in their functions. Titanium implant is preferred because it has low density (4.5g/cm^3) compared to stainless steel (7.9g/cm^3 for 316) and 8.3g/cm^3 and 9.2g/cm^3 for cast CoCrMo or CoNiCrMo forged), good mechanical and chemical properties. According to some authors, titanium alloys are better tolerated than pure titanium, since the oxide layer formed has a larger thickness (10-20μm) which is regenerated every nanosecond. Stainless steel is categorized as widely used in the past because they were cheap, durable, easily obtained and processed. Decrease in carbon content and addition of moliben (316L grade steel) had the effect of increasing the corrosion resistance. Another large group of alloys used to make implants and prostheses are Co-Cr alloys (or stellites). Chromium is the main alloying element that increases corrosion resistance and oxidation by the formation of oxide film (Cr_2O_3) on the surface. Co-Cr alloys exhibit characteristics similar to the stainless steels and have the advantage of practically zero toxicity.

We studied the corrosion behavior of the alloy Co-Cr (the metal material used in biomedical applications, fig.1) in aqueous solution with different pH, because it is known that all vital processes in the body is carried out in the exact values of pH. Were selected three types of media, so-called artificial saliva with different pH values: Hank (pH 7.4), artificial saliva Saliva Fusayama Meyer (pH 5.0) and Ringer's saliva (pH 6.6). The electrochemical cell used during the experiment is made up of the working electrode (WE) - Co-Cr alloy, reference electrode Ag / AgCl (saturated KCl solution, E = 200mV/NHE) (RE), the auxiliary electrode (EC)- Pt-Rh grid. After corrosion tests carried out in the four solutions / artificial saliva, the samples were subjected to microscopic analysis. Areas with aspects of localized pitting corrosion phenomenon highlighted the qualitative analysis by electron microscopy (SEM - Scanning Electron Microscope, fig.) were further investigated specific techniques EDS equipment - Energy-dispersive X-ray spectroscopy quantitative analysis (Fig.2, Fig.3). The fields that indicate susceptibility of alloy studied was revealed: the chemical composition of the alloy examined, variation of concentration of an element in a particular area of interest (pitting)- three dimensional version of the distribution of chemical elements over an area that includes the points of corrosion.

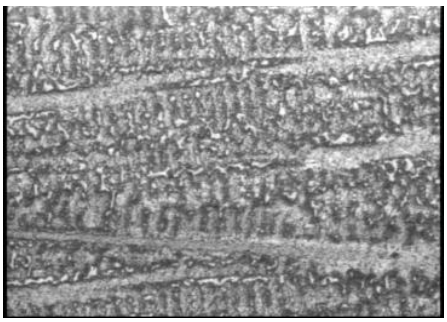
***Table 1.** Chemical composition and mechanical properties of Co-Cr alloy [10, p.67]*

Chemical composition, %									
Specification	EN 10204 -3.1B	Co	Cr	Mo	Mn	C	Fe	Si	Sonstige
	max. [%]	63	29.4	5.95	0.6	0.29	0.05	0.7	0.1

Properties		
Density	**Hardness**, HV10	**Modulus of elasticity, E**
[g/cm^3]		[MPa]
8,3	420	230,000



X100



X 500

***Fig. 1.** Microstructural aspects of CoCr dental alloy samples (optical microscopy) [10, p.68]*

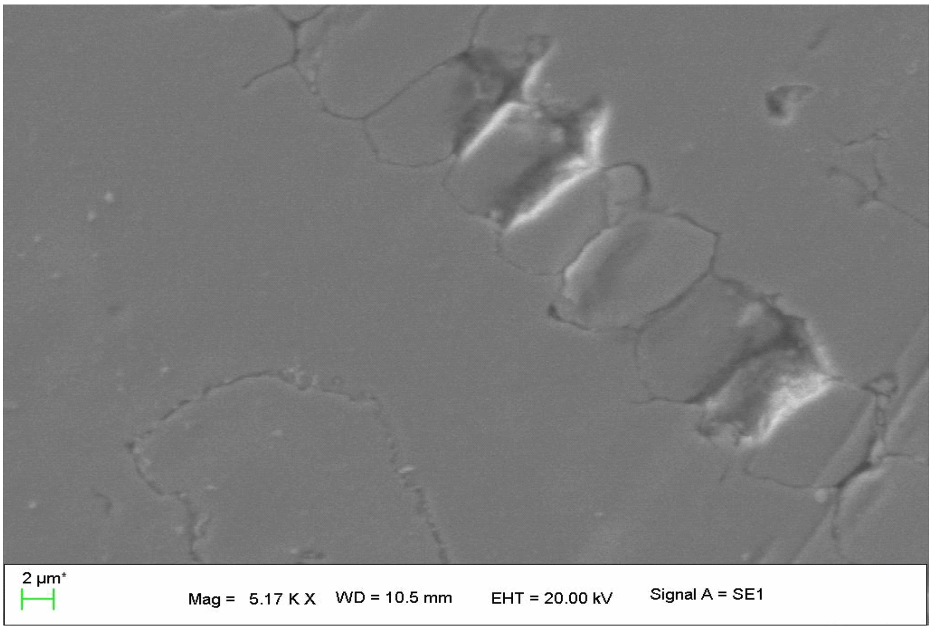
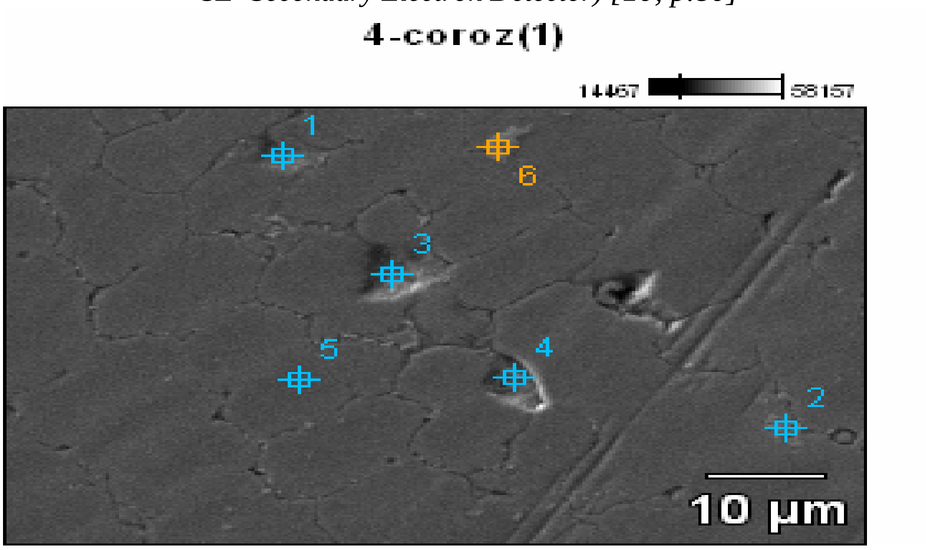
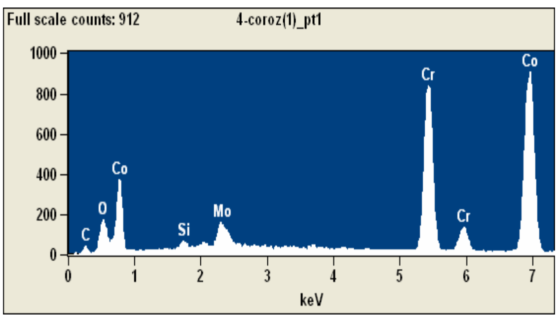
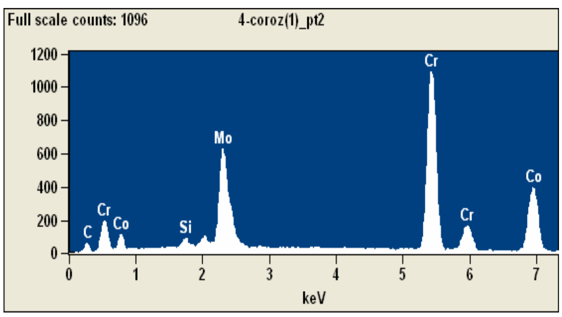


Fig. 2. *CoCr dental alloy /Micrographic issues - details of areas affected by corrosion (pitting) (Magnification: 5000 X, using detectors BSE - Back-Scattered Electron Detector and SE- Secondary Electron Detector) [10, p.80]*







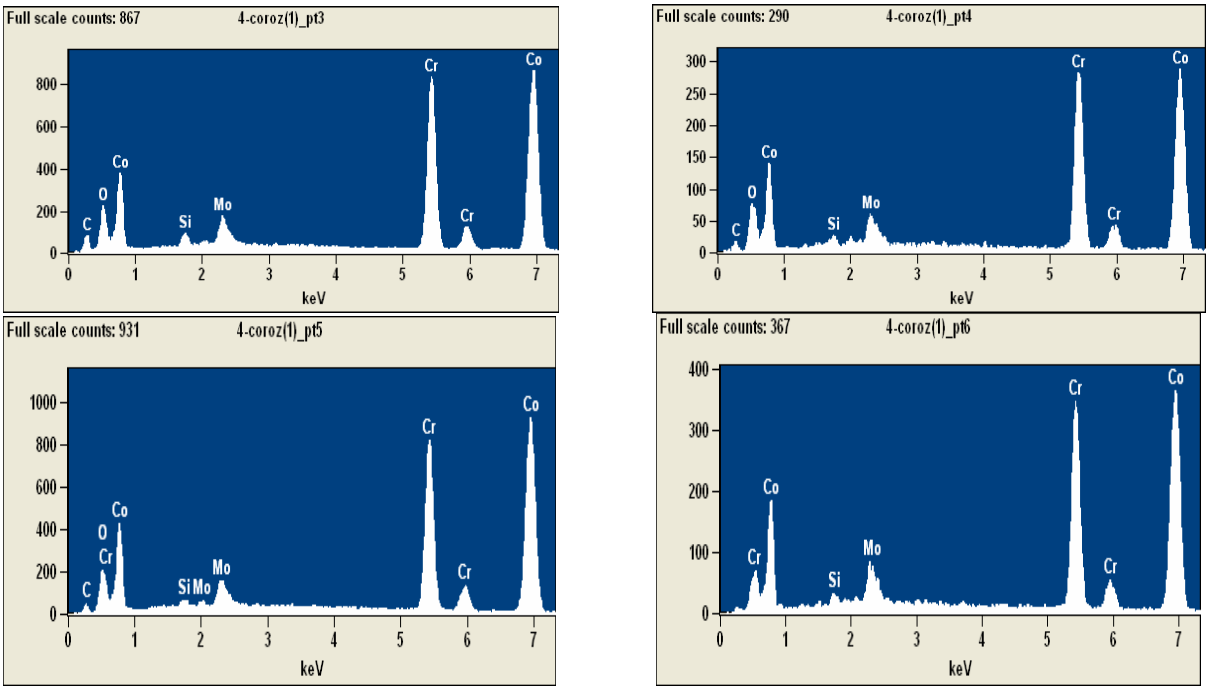


Fig. 3. *CoCr dental alloy (sample 4)/*
The pitting areas revealed by the quantitative analysis with SEM

Table 2. *Corrosion rates of biomaterials in Hank's solution [8]*

Alloy	**Metal transformed into compounds**	**Metal found in tissue**
	[ng/m²h]	[ng/m²h]
Stainless steel - polished mechanically (AISI 316L) - chemically polished	7.8 230	0.274 -
Vitalium - mechanical polishing alloy (Co-Cr-W-Ni), the chemical polishing	150 20	0.249 -
Ti - mechanical polishing - chemical polishing	4.1 3.5	0.430 -
Ti-16Mo	1.5	-
Ti-5Ta	0.26	-

Table 3. *Potential drops in Hank's solution and time repassivation of metallic biomaterials in 0.9%NaCl [8]*

Metallic biomaterials	**Potential drops**	**Repassivation time**			
		t^{c}		$t^{0,05}$	
	[V]	[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. Comparative study of biological properties of some metals and alloys used in dentistry

Biomaterial surface reactivity and living tissue response are measured by the degree of biocompatibility. From this point of view, biomaterials can be: biotolerante (e.g. bone implant is separated by a layer of soft tissue) bioinerte (they do not cause migrations of ions in living environment they do not influence biochemical living cells do not lead to rejection phenomena), bioactive (connection between implant and tissue is made without the use of binders).

From the literature we can draw some general questions relating to metallic biomaterials toxicity, as follows:

Aluminum negative influence on bone metabolism in that it inhibited the phosphorylation and ATP synthesis, thereby reducing cellular energy reserves. Regarding alumina (Al_2O_3), the main compound of aluminum, we can say that it has no toxic effect due to its low solubility, even promoting cell proliferation. Cobalt is considered an essential element of life. After nickel and cobalt chrome stands between allergenic metals.

Chromium and it also belongs to the group of elements essential to life. Toxicity depends on the oxidation state in which it is located. Hexavalent chromium is more toxic than trivalent chromium and is considered a potent mutagen and carcinogen. Trivalent compounds do not penetrate through the skin or cell membrane and bind to the stable protein complex. In contrast, hexavalent compounds have a greater power of oxidation of organic molecules, passing easily through cell membranes and are reduced to the more stable trivalent form, which penetrates the nucleus and induce mutations in DNA interactions.

Nickel is one of the most studied factors related to effects on the human body. He ubiquitous in our environment and is absorbed inland digestive, respiratory, skin or metal implants, inhalation, implantation, ingestion, intraperitoneal injection, intramuscular or intravenous. The amount of nickel in blood and urine is an accurate indicator of intoxication with this metal. Nickel has high affinity for microsomal and mitochondrial proteins of pneumocytes, which are mainly based on energy storage cell reserve and location of complex enzyme systems. Nickel compounds such as Hydrocarbonate, sulfides or oxides of nickel activate interleukin production and lipid peroxidation, thus generating free radicals, which are potentially highly carcinogenic. Nickel is considered as the most sensitizing metal soft tissue. It leads to allergic contact dermatitis, allergic reactions producing more alergies than all other metals combined. Vanadium lowers concentrations of coenzyme A and Q by disinhibition oxidative phosphorylation, interferes with many enzyme systems and can induce irreversible disruption. High solubility contributes to the toxic effects that are estimated to be 10 times larger than the Ni-Co-Cu complex. Aluminum and vanadium elements are released into tissues. Metal ions released from corrosion and wear can induce hearing loss after a long period of implantation, especially because of the potential adverse effects of vanadium. Release of vanadium ions in the body can produce serious organ damage and, also, can produce platelets systems. For this reason it is preferable alloy Ti-Al-Nb-Ti alloy instead of Al-V. In vitro studies showed that the cells behave differently in the presence of debriurilor generated by the wear of the two alloys. So there is an increased release of prostaglandin E2 in response to contact to Ti-6Al-4V particles, and an increase in the release of other inflammatory cytokines compared with Ti-Al-Nb particles. These data suggest that Ti-6Al-4V stimulates phagocytic cells more than the Ti-Al-Nb and Ti easily. Exposure of bone marrow cells from Ti-6Al-4V particles induce a significant increase in the release of proinflammatory and osteolytic mediators that are responsible for the lost prostheses.

4. Conclusions

Research conducted and thorough documentary study allow drawing general conclusions regarding biocompatibility but also the limits of metals and alloys used in dentistry:

- Metallic biomaterials are the most popular class of materials for implants, prostheses and medical instruments, due to their very good mechanical properties and acceptable biocompatibility.
- The main aspects that must be considered when using metallic materials in dentistry applications include corrosion, release of heavy metal ions, attrition and lack of elasticity. From this point of view we can speak clearly about the proven tissue toxicity of stainless steel in contact with human tissue. The problems raised by these steels in use as biocompatible materials are associated with the release of nickel ions, in particular as a result of the corrosion of corrosion products release causes inflammatory reactions, which prevents the endosseous implants osseointegration and favors the formation of fibrous capsule.
- Modern Co-Cr alloys due to superior mechanical properties and cost price advantages have replaced the noble class IV alloys in conventional technology (metal-polymer) and modern (metal and metal-ceramic composite) alloy cobalt - chromium -

molybdenum were used as subperiosteal implants, plates and implants endosseous transosseous, the advantage of mechanical biocompatibility better than stainless steel (316L), biocompatibility comparable to their chemical and, particularly, the lack of toxicity.

- Some common applications for metals, titanium has the best biocompatibility, surface explained by the formation of a stable oxide thin film, which confers passivity, it is preferred that the implant material due of density low mechanical properties and very good chemical;
- Titanium alloys are better tolerated than pure titanium because the oxide layer that forms is much larger (10-20μm) has been shown as corrosion resistance, biological compatibility, features and price resistance, the most used in medicine are alloys "conversion" on the basis of titanium. Their corrosion resistance can be increased by alloying with molybdenum, zirconium, rhenium, niobium, chromium, manganese, titanium alloy Ti-6Al-4V commonly used in implants shows a combination of the most favorable characteristics, but the problem of metal ion release.

Aluminum and vanadium are released into the tissue elements, metal ions released from corrosion and wear can induce hearing loss after a long period of implantation, especially due to the adverse effects of vanadium.

References

[1]. Anderson JM, et al. - *Host reactions to biomaterials and their evaluation*, Ratner BD, et al., eds. Biomaterials Science: An Introduction to Materials in Medicine. London: Elsevier, 2004

[2]. ASM Handbook Committee - *Metals Handbook-Corrosion of Metallic Implants and Prosthetic Devices*, vol. 13, ninth ed., American Society for Metals, Metals Park, 1987

[3]. Christoph Leyens, Manfred Peters - *Titanium and Titanium Alloys-Fundamentals and Applications,* Ed. WILEY-VCH, pg. 4-16, 2004

[4]. Gotman I. - *Characteristics of metals used in implants*, J Endourol (1997), 11(6):383-9

[5]. Claudia Fleck - Dietmar Eifler - *Corrosion, fatigue and corrosion fatigue behaviour of metal implant materials, especially titanium alloys,* International Journal of Fatigue 32 (2010) 929–935

[6]. M. Karthega, V. Raman, N. Rajendran - *Influence of potential on the electrochemical behaviour of b titanium alloys in Hank's solution*, Acta Biomaterialia 3 (2007) Elsevier, p. 1019–1023

[7]. H.J. Rack, J.I. Qazi - *Titanium alloys for biomedical applications*, Materials Science and Engineering C 26 (2006) Elsevier, p. 1269 – 1277

[8] Ghiban, B. - *Metallic Biomaterials* - Ed. Printech Bucuresti (1999)

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