INTRODUCTION TO METALLIC BIOMATERIALS

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ABSTRACT

The paper presents a bibliographic study about the metallic biomaterials, synthesizing the aspects related to properties, applicability, obtaining methods. Biomaterials can be used as medical devices, implants and prostheses. The metallic biomaterials are classified, by chemical composition and structure, in: pure technical metals, metallic alloys and composites with metallic matrix. The material quality of an implant must respect the following criteria: biochemical criteria and biomechanical ones. According to the biochemical criterion, the applicability of a material is determined by its biocompatibility, and from the biochemical criteria, it is determined by the fatigue resistance, the most important parameter, but not the only one.

KEYWORDS: biomaterial, alloys, nickel, chrome, steel, biocompatibility

1. Introduction

A biomaterial can be defined in two ways: a synthetic material used to replace a part of the human body or to function straight with a living tissue or an inert biological substance destined for implantation in the living systems [1].

The successful usage of a biomaterial depends on 3 main factors as:

- properties and biocompatibility;
- health state of the patient;
- the efficiency of the surgeon who uses the implant.

According to the chemical composition and physical structure, the metallic biomaterials are classified in:

- pure technical metals;
- metallic alloys;
- composites with metallic matrix.

Table 1. *Biomaterials classification*

Medical device	Implant	Prosthesis	Surgical alloy	Artificial organ	Biocomposite

A. Metals are used in medical field, currently, as surgical implants, as dental materials and in the making of different devices.

There are over 30 metallic elements used in medicine in the shape of:

- implants and orthopedics and dentistry prosthesis: Al, Co, Cr, Fe, Mn, Mo, Nb, Ni, Sn, Ta, etc.;
- precious and semiprecious dental alloys with: Ag, Au, Cu, Ga, In, Ir, Pd, Pt, Rh, Ru, Sn, Ti, Zn, etc.;
- non-precious dental alloys: Al, B, Be, Cd, Co, Cr, Fe, Mn, Mo, Ni, Si, Ti, V, W.

B. Alloys used like surgical implants in orthopedic and dentistry, are divided in:

- austenitic stainless steels;
- cobalt base alloys;
- titanium base alloys.

The most used alloys are the ones based on cobalt – chrome (cca. 70%), followed by titanium alloy; the last one has excellent biocompatibility properties [2, 3]. The dental alloys used for dental rehabilitation:

- crowns and connecting decks;
- glued porcelain on metallic alloys;
- wires for correcting teeth;
- metallic teeth from dental alloys;
- alloys for brazing dental works.

There are over 1000 dental alloys, which are classified in 4 subgroups:

- precious alloys with Au, Pt, Ag content;
- semi-precious alloys with low Au content, but based on Pd;
- non-precious alloys from stainless steel, Co-Cr and Ni-Cr group;
- titanium base alloys.

C. Composite materials with metallic matrix – to which belong:

- dental amalgam with Hg and Ga matrix;
- cermets materials;
- prosthetic components covered with different ceramic layers.

The superficial layers deposited on implants gives them special properties like: corrosion resistance, esthetic aspect, hardness and facilitates the development of the living tissue in the area [4].

2. Aspects regarding metallic biomaterials

2.1. Titanium and its alloys

Titanium is an active element chemically wise and should corrode strongly in ambient conditions.

In reality this phenomenon does not manifest due to TiO_2 protector layer on its surface.

At air heat, titanium and its alloys strongly interact with the gases from the atmosphere, resulting chemical combinations, which forms the protector layer. When the temperature rises, the oxidation speed intensifies and the possibilities of an explosion happen. Also, the titanium mixes with the nitrogen and hydrogen, forming nitrides and hydrides [5].

Due to small density, associated with good mechanical properties, micro-alloyed titanium and its alloys are superior to the other metallic materials, having a higher resistance (30-40 daN/mm^2) reported at density, which is superior to higher alloyed steels (15-35 daN/mm^2).

Table 2. *Classification criteria of titanium*

After processing	Plastic deformable alloys
	Cast alloys
After properties	High plasticity and medium resistance alloys
	Enough plastic and high resistance alloys
	High corrosion resistance alloys
	Super plastic alloys
	Amorphous alloys
	Shape memory alloys
After the usage field	For welding constructions
	For aviation and space technique
	For chemical industry
	For prosthetic devices
After structure	Alloy with Tiα structure
	Alloys with $\alpha+\beta$ structure (biphasic)
	Alloys with Tiβ structure

Titanium alloys which are used in surgical implants manufacture are Ti6Al4V. In specialty references there also appears titanium alloys: TiSnMoAl and Ti13V11Cr3Al.

The TiSnMoAl alloy are known under HILITE 50 commercial name and contain 4 %Al, 2 %Sn and 4 %Mo, difference Ti and are characterized by a high usage resistance.

Table 3. *Chemical composition of Ti6Al4V alloy*

Al	V	Fe	Other elements		C	Ti
5.5-6.5	3.5-4.5	max 0.25	0.1 each	0.4 total	max 0.08	Difference

Because of the high melting temperature, and also the sudden increase of chemical activity with the temperature, titanium alloys are elaborated in electrical arc furnace and through induction, only in protective atmosphere with vacuum or inert gases [6].

2.2. Cobalt – chrome cast alloys

These alloys are open to oxidation during melting, and cast alloy is fragile and hard. The alloy has a high melting temperature.

The cooling contraction is 1.9% and makes it difficult to achieve the dimensional accuracy asked by the pattern [7].

Because of that, these alloys are not recommended for precise castings, like teeth crowns or connecting decks, meanwhile their use as a support for melted porcelain is not recommended due to the oxidation suffered by the alloys at work temperature.

Nevertheless, the materials have a good corrosion resistance and are highly tolerated in the mouth cavity.

Table 4. *General composition of a Co-Cr biomaterial*

Co	Cr	Mo	C	Ni
65%	25%	5%	0.2-0.35	difference

The chrome percentage improves the oxidation resistance of the alloys; if the value is over 30%, it will lead to difficulties at casting.

The cobalt increases the elasticity modulus, resistance and hardness higher than nickel.

The safest way to increase the Co-Cr alloys properties is to increase the carbon content. A change of only 0.02 %C modifies the properties in such a way that the alloy cannot be used in stomatology.

In medicine the Co-Cr alloys are used as implantable devices. The Co-Cr alloys are metastable and crystalize in CFC system, and the carbides are present at grains boundary.

The melting temperature is situated between 1250-1450 ºC and is over the melting capacity realized by a natural gas flame; their melting in electromagnetic induction furnace is recommended.

2.3. Nickel – chrome cast alloys

Ni-Cr alloys gained the attention of researchers with the limitations discovered at Co-Cr alloys: low ductility, high contraction at solidification and a rise tendency to oxidation.

In the industry, these alloys are known as NIMONIC and have applications in reaction engine technology.

Table 5. *General composition of a Ni-Cr biomaterial*

Ni	Cr	Mo	W	Mn	Be	C
68-80%	10-25%	0-13%	0-7%	0-6%	0-2%	0.1-0.2%

With these elements we can find small amounts of Al, Ti, Co, B, Si. These alloys are excellent as a support for melted porcelain.

The alloys crystalize in CFC system, and the cast material has a structure with big grains which indicate a dendritic structure.

The solidification contraction is 1.5%, and the alloys melt naturally in induction furnaces and are casting in phosphatic forms.

Because of the low temperature field, the Ni-Cr alloys provide a more precise casting which make the connecting decks and dental crown to have minimal flaws.

2.4. Silver-palladium cast alloys

Silver and palladium present total solubilization.

While Pd has a high affinity for H_2 and a high melting temperature (Ttop = 1552 °C), Ag has a lower temperature and is appropriate for base alloys casting.

The cast Ag-Pd alloys are Ag-Pd-Cu ternary system, which can be multi-phasic or mono-phasic.

To theses alloys, we can apply hardened heat treatments through precipitation.

Table 6. *General composition of a Ag-Pd biomaterial*

Ag	Pd	Cu	Au	Zn
45%	25%	15%	14%	1%

These values can vary according the required precision of final element.

The cast precision takes in consideration the attention with which the melting is made, and also its realization in controlled atmosphere.

Materials can be used as a support for melted porcelain, but we have to keep in consideration the porcelain affinity for silver, which leads to obtain a greenish color of them.

The alloys can be hardened through precipitation when the melted porcelain is deposit on them.

2.5. Stainless steels

The first stainless steel used in metallic implants was AISI 302 steel, which is harder than vanadium steel and has good corrosion resistance properties.

The vanadium-alloyed steel cannot be used, because it has an inadequate corrosion resistance.

After, it was introduced AISI 302 steel alloyed with molybdenum to improve the corrosion resistance in salt water. This alloy is AISI 316 steel.

The carbon content was reduced from 0.08% to 0.03%, to obtain a good corrosion resistance in chlorine solution.

The steel becomes AISI 316L steel.

Chrome is a major element in corrosion resistant stainless steels. The minimal concentration is 11%. Chrome is a reactive element, but its alloys can passivate, having an excellent corrosion resistance

Table 7. *Chemical composition of AISI 316 and AISI 316L stainless steels*

%	C	Cr	Ni	Mo	Mn	Si	P	S	Fe
AISI 316	0.006	17-20	12-14	2-4	2	0.75	0.03	0.03	Rest
AISI 316 L	0.002	17-20	12-14	2-4	2	0.75	0.03	0.03	rest

These stainless steels can be used for metallic implants.

They cannot be hardened through heat treatments but can be hardened through cold processing.

The AISI 316 steel is nonmagnetic and presents a higher corrosion resistance than another stainless steel, also molybdenum alloying increases pitting corrosion resistance in salt water.

Although it is known like a toxic element, nickel is found in chemical composition like alloying element which stabilizes the austenite at ambiance temperature and more, increases the corrosion resistance [8, 9].

The austenite stability at low temperature is also influenced by the chrome content.

The austenitic stainless steels suffer a gardening process in exploitation, that being the reason why it cannot be cold processed without intermediary heat treatments.

The heat treatment cannot determine the appearance of chrome carbides at grains boundary, carbides which can cause the corrosion phenomena formation.

ASM International recommend the AISI 316L steel usage to implants manufacture.

In stomatology, the stainless steels are used to fabricate wires and crowns for partial teeth.

3. Conclusions

Biomaterials release ions and metallic particles in the human body, which will concentrate in urine, blood, nails, hair and tissue around implants.

There is danger for allergic reactions or immunological and inflammatory reactions.

The dental alloys based on precious or semi-precious metals are inert and perfectly biocompatible.

Out of biomaterials, titanium and its alloys are the materials which correspond to mechanical, chemical and biological requirements.

Some metals like beryllium, nickel and mercury are already considered prohibited in the human body. Nickel is considered one of the most dangerous metals used like biomaterial.

The metal effects like chemical element are different from its compounds, oxides and organic compounds; these increase the risk of pathological reaction production in human body.

It is recommended the usage of implants or prosthesis superficial covered with various protective films, which are inert to the human body and sometimes can facilitate the development of bone cells.

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