New Metallic Alloys Used for Dental Implants Manufacturing

Diana-Irinel Băilă

***Abstract*—Trauma, degeneration and diseases often make surgical repair or replacement necessary. When a person has a joint pain, the main concern is the relief of pain and return to a healthy, normal and functional life style. This usually requires replacement of skeletal parts that include knees, hips, finger joints, elbows, vertebrae, teeth and repair of the mandible. Biomaterial is available and suitable for inclusion in systems which augment or replace the function of body tissues or organs. From as early as a century ago, artificial materials and devices have been developed to a point where they can replace various tissues of the human body. These materials are capable of being in contact with body fluids and tissues for prolonged periods of time, with little or without any adverse reactions. In this paper, there are presented new biomaterials that can be used to manufacture dental implants and restorations, like Fe alloys, Co alloys, Ti pure and Ti alloys, Ti-Ta alloy, Ni-Ti alloy, zirconium alloy.**

***Index Terms*—Dental implants, biomaterials, iron alloys, Co alloys, Ti alloys.**

I. Introduction

In function of structure and properties of the metallic implant, the materials are selected according to the manufacture process.

With exception of noble metals such as gold (which do not represent a major fraction of implant metals) the majority of used alloys are different chemical combinations with other elements, as in the case of metal oxides.

The most used alloys are rutile TiO_2 and ilmenite $FeTiO_3$ [1]-[3].

The purity grade of the titanium product is very important for dental implants [1].

In the production of the most common grades of commercially pure (CP) titanium, these grades differ in oxygen content by only tenth of a percent, yet these small differences in oxygen content have a an important impact regarding the mechanical properties: yield, tensile and fatigue strength of titanium.

In the case of multicomponent metallic implant alloys, the raw metal product will usually have to be further processed both chemically and physically [1]-[6].

Processing steps include remelting addition of specific alloying elements and controlled solidification from the melt. Thus, it is obtained an alloy that meets sure chemical and metallurgical specifications.

A metal supplier will typically further process the bulk raw metal product (alloy and/or pure metal) into stock bulk shapes, such as bars, wires, sheets, rods, plates, tubes or powders [6].

The materials used for dental implants have evolved significantly in the last 50 years.

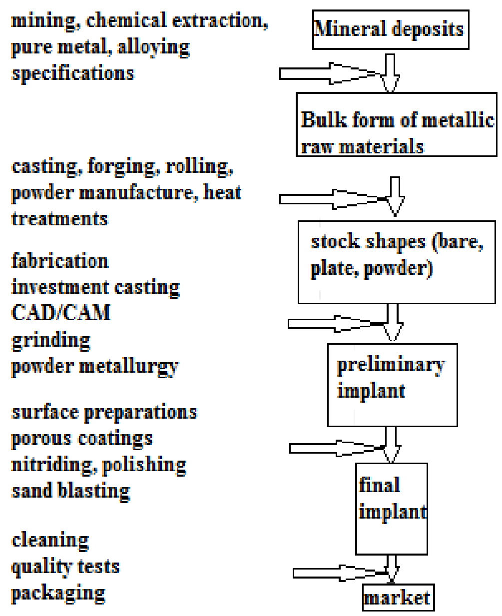

Fig. 1. Processing steps of a typical dental implant [1].

Over time, the first materials were the metal from the austenitic stainless steels, Co-Cr alloys or at the titanium base, currently considered to be biocompatible, followed inert ceramic biomaterials and bioactive biomaterials, with their advantages and disadvantages.

One of the major disadvantage is that the use of synthetic materials in hard tissue cause the bone retracted to the implantation area, but this is happening in few years [7], [8].

Figure 1 illustrates the processing steps of a typically dental implant, from mining the metal to fabrication and launch on the market.

About the material's characteristics, the Young modulus exceeds 350 MPa in case of ceramics and 200 GPa for stainless steels and alloys Co-Cr even Ti has the modulus over 100 GPa, in case that the mature human bone has a module between 7 and 30 GPa [1], [9]-[12].

Manuscript received October 23, 2016; revised April 3, 2017. This work has been funded by University Politehnica of Bucharest, through the "Excellence Research Grants" Program, UPB – GEX. Identifier: UPB–EXCELENȚĂ–2016 Research project title "Experimental researches concerning new biocompatible materials manufacturing by DMLS process used for personalized dental implants and restorations / Cercetări experimentale privind utilizarea de noi materiale biocompatibile destinate implanturilor și restaurărilor dentare personalizate fabricate prin sinterizare DMLS", Contract number 29/26.09.2016.

Diana-Irinel Băilă is with the University Politehnica of Bucharest, Blv. Splaiul Independentei, 313, Sector 6, cod 060042, Romania (e-mail: baila_d@ yahoo.com).

TABLE I: CHEMICAL COMPOSITION OF METALS USED FOR IMPLANTS [1].

Biomaterial	Nominal composition elements	Tensile Strenght [MPa] minim	Elongation [%] minim	Specifications
Iron Fe alloys	Fe-18Cr-2.5Mo	480	30	Cast and wrought forms
	Fe-18Cr-14Ni-2.5Mo	150-1350	10-40	
	Fe-Zr-10Ni-3Mn	24-1100	10-35	
	Fe-15Ni-2.5Mo	490-860	4-40	
	Fe-22Cr-13Ni-5Mn-2.5Mo	690-1035	12-35	
	Fe-23Mn-21Cr-1Mo	827-1379	12-30	
Co alloys	35Co-35Ni-20Cr-10Mo	241-1580	3-60	Cast and wrought forms
	Co-28Cr-6Mo	655-1192	8-20	
	40Co-20Cr-16Fe-15Ni-7Mo	1240-2275	1-65	
	Co-20Cr-15W-10Ni	190-896	20-45	
Ti and Ti alloys	99Ti (grade I-IV)	240-550	4-30	Cast and wrought forms
	Ti-6Al-4V	860	8	
	Ti-6Al-4V (ELI)	825-860	8-10	
	Ti-6Al-7Nb	800	10	
	Ti-13Nb-13Zr	560-860	8-15	
	Ti-12Mo-6Zr-2Fe	931	12	
	Ti-15Mo	690-724	12-20	
	Ti-3Al-2.5V	621-862	10-15	
Tantalum	99Ta	172-517	12-30	Deposit and wrought forms
Zirconium alloy	Zr-2.5Nb	450	15	Wrought forms
Nickel Titanium alloy	45-57Ni-Ti	551	10	Wrought forms

This will certainly impose that future research in this area should be oriented towards obtaining new biocompatible materials which have a Young's modulus much more similar to that of bone [1], [9]-[12].

The chemical composition of metals used for implants are presented in Table I.

II. IRON ALLOYS USED IN DENTISTRY

The outcome of biomaterials and medical devices implantation is not always optimal, many times owing to suboptimal tissue-biomaterials interactions for bio-compatibility.

Implants can be retrieved after in vitro studies or at either reoperation or necropsy/autopsy of animals or humans, and they may or may not failed.

The correlation of biomaterials surface chemistry with performance is a critical step.

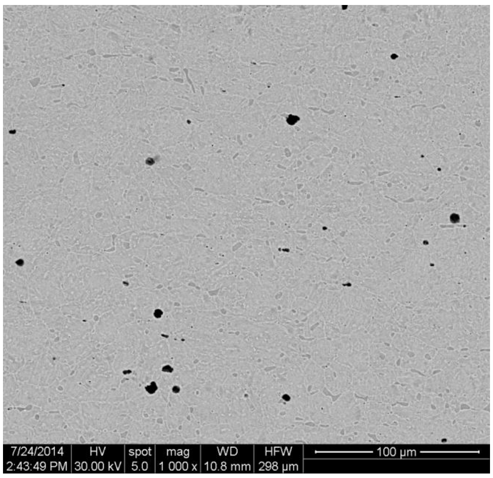

Fig. 2. SEM realized on probe Fe-Cr (x1000).

Fig. 2 and Fig. 3 present electron microscopy on the stainless steel Fe-Cr probe and it can be remarked the presence of homogeneous martensitic structure and fines grains of δ ferrite and small black inclusions of Si oxides.

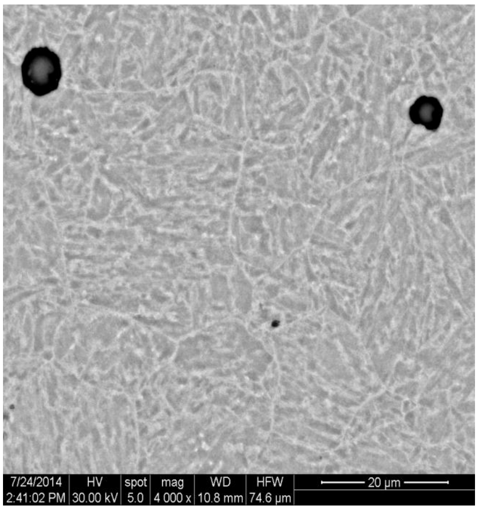

Fig. 3. SEM realized on probe Fe-Cr (x4000).

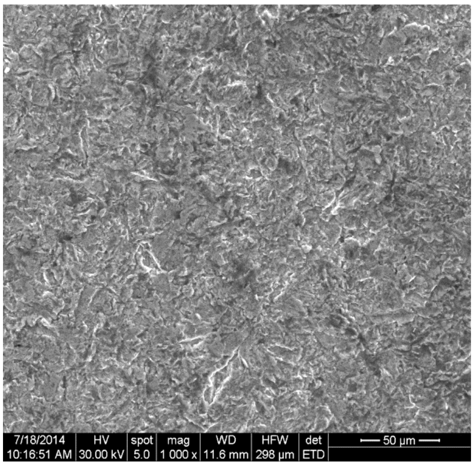

Fig. 4. SEM realized on probe Fe-Cr-Ni (x1000).

The classic Fe-Cr-Ni alloy is used frequently in dentistry and presents good mechanical resistance, but the time to obtain the dental crown is too long because of rectification operations.

Thus, all the patients lose more time to obtain an adequate dental crown.

In Fe-Cr-Ni alloys (microscopy probes in Fig. 4 and Fig. 5) may appear some tensions after classical sintering process.

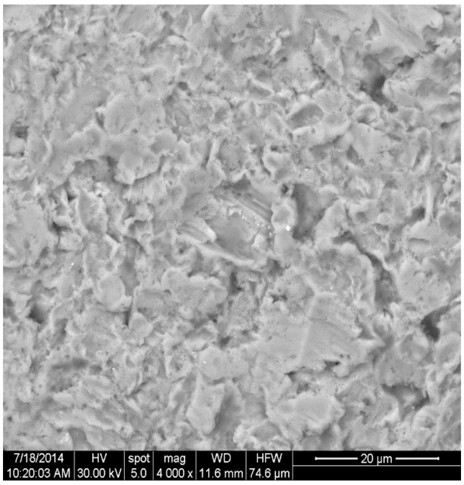

Fig. 5. SEM realized on probe Fe-Cr-Ni (x4000).

In the last years, the implant research guided the development of new and modified implant designs and materials, assistance in decisions of implant selection and management of patients.

Also, it was the base and permitted many studies of the mechanisms of biomaterials-tissue interactions.

Preclinical tests of modified designs and materials are crucial to developmental advances.

These investigations usually include in vitro functional testing and insertion/implantation of the implant in the intended location in an appropriate model, followed by noninvasive and invasive monitoring, specimen explantation and detailed pathological and material analysis.

Animal investigation may permit more detailed monitoring of implant functions and enhanced observation of morphologic detail, using frequently tests of laboratory parameters and allow in situ observation of fresh implants at desired intervals.

Animal tests present facility observations of specific complications in an accelerated timeframe.

The animal models that faithfully duplicate the relevant human anatomy, physiology and pathology are not often available.

III. Cobalt Based Alloys

Co based alloys include ASTM F75 and F90, forged Co-Cr-Mo alloy ASTM F799 and multiphase MP35N alloy ASTM F562.

Fig. 6. Analogue implants of Co-Cr.

Alloy powder Co-Cr (ST2724G) is used in medicine for realization of dental crowns, analogues implants (Fig. 6), dental bridges and implants [9]-[11].

TABLE II: Mechanical Properties of Co-Cr alloys

Mechanical properties	Value
Elastic limit (0,2%) RP 0,2	817 MPa
Break elongation	9,7%
Vickers hardness	375 HV5
Elastic modulus	228,7 GPa
Volume mass	8,336 g*cm^{-3}
Corrosion resistance	<4 µg/cm^2
Thermal expansion coefficient	14,5*10^{-6} K^{-1}

Mechanical properties of alloy powder Co-Cr are given in the Table II below.

The chemical composition of Co-Cr alloy (ST2724G) is as follows: 54.31% Co; 23.08 % Cr; 11.12% Mo, 7.85% W, 3.35% Mn, Si and Fe < 0.1%.

Powder of Co-Cr is a tolerable material in medicine and the powder alloy Ti-6Al-4V is tested as biocompatible material.

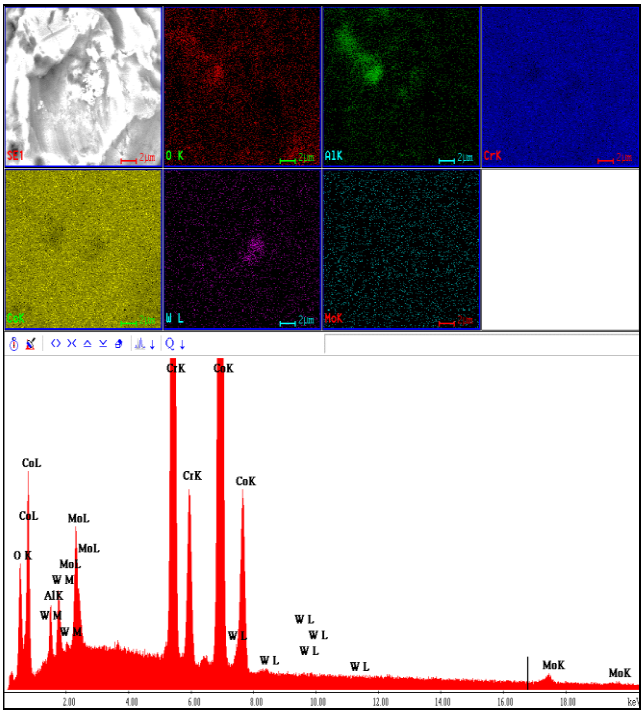

Fig. 7. Mapping of Co-Cr sintered by DMLS.

In Fig. 7 is presented the mapping of Co-Cr alloy sintered by DMLS process used for analogue implants manufacture.

Mechanical properties of Co-Cr alloys are presented in Table II.

IV. Titanium Based Alloy

Dental implants differ greatly by the material from which they are made, shape and geometry, number and shape the end turns, and connection.

The two most common titanium-based implants are commercially pure (CP) titanium (ASTM F67) and Ti-6Al-4V alloy (ASTM F136). F67 alloy present 98.9-99.6% Ti.

Fig. 8 presents a 3D model for a mandible realized by 3D Printing. Fig. 9 and figure 10 present a SEM analysis of mandible fracture Ti-20%HA. Fig. 11 presents a EDS analysis of mandible fracture Ti-20%HA [11].

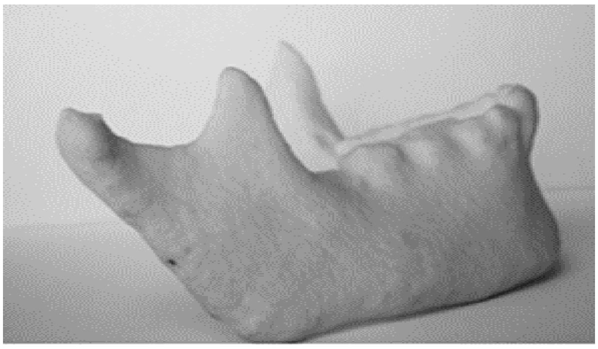

Fig. 8. Mandible 3D model realized by 3D Printing.

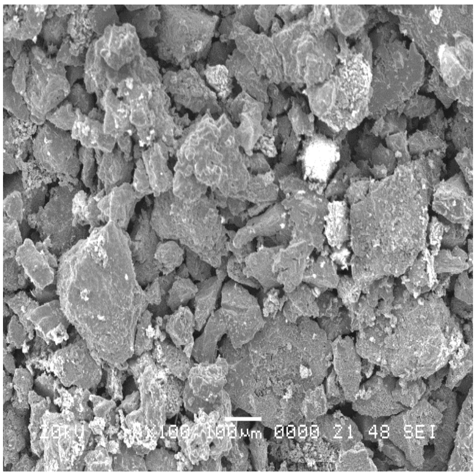

Fig. 9. Mandible fracture Ti-20%HA (x1000).

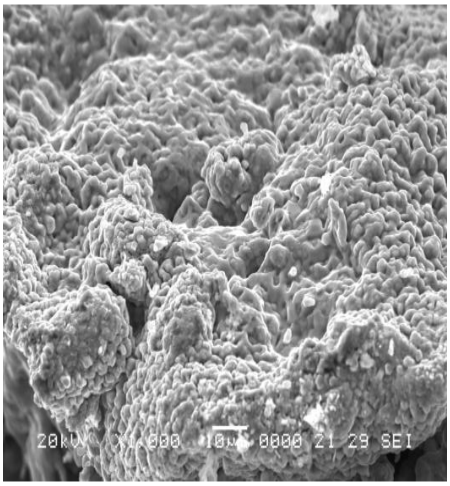

Fig. 10. Mandible fracture Ti-20%HA (x1000).

Table III presents the mechanical properties of Ti alloys.

Metallic implant with trabecular structure is the latest innovation in the field of dental implantology, being the only implant with three-dimensional (3D) structure, like the Ti-Ta alloy.

Tantalum is a metal with a very high biocompatibility and a high corrosion resistance and is manufactured by EBM thermal process.

Elemental tantalum is deposited on a substrate with atom by atom creating a three dimensional surface nanotexturate (3D) strictly controlling the porous implant area specifications. Through this process there are used special physical and biological properties of tantalum to create a unique material with a structure and rigidity similar to those of human cancellous bone.

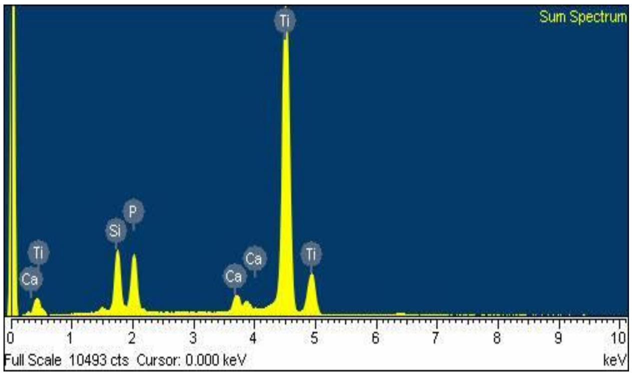

Fig. 11. EDS analysis in mandible fracture.

TABLE III: MECHANICAL PROPERTIES OF TI ALLOYS

Ti alloys	**Young's modulus [GPa]**	**Yield strength [MPa]**	**Tensile strength [MPa]**	**Fatigue Endurance Limit strength (at 10^7 cycles) [MPa]**
F67	110	485	760	300
F136	116	896	965	620

Osteointegration is the growth and healing of bone implant inside and outside ensuring much greater surface contact between implant and bone body than normal titanium implants.

Metallic implant with trabecular structure has become the treatment of choice when solving difficult cases and greatly increasing the success rate.

Its structure similar to human bone spongy (porous), interconnected porosity and bone growth potential among these pores are a unique combination of features that contribute to osteoconductivity the metal implant with trabecular structure, which leads to the formation of vascular bone on and in implant surface.

Another new alloy of titanium and zirconium is a material intended solely for dental implants. Ti-Zr alloy is fifty times more resistant than the current material, titanium.

The results of the experiment conducted in the clinical trial showed that the implant from Ti-Zr was integrated much better bone structure than titanium.

Another potential advantage met is the potential use in bone structure, where normally the process of implantation is complicated, requiring an augmenter processes. Interest in searching for high-performance materials appeared with titanium.

V. CONCLUSIONS

Through our research, we identified the major problems being the metallurgical principles underlying structure-property relationships, design, production and proper utilization of the implants.

The alloys Co based and Ti based present very good mechanical properties, being resistant to corrosion tests and are biocompatible materials.

These materials can be used successfully to manufacture dental implants, orthopaedic hips, knees, oral/maxillofacial implants, stents and heart valves.

Any metallic implants will differ after the manufacture process, metallic alloys and its properties.

Functional, aesthetic and health compromises have been correlated with the loss of oral dentition.

Actually, there exists a multitude of dental implant designs and intraoral restorations, depending on their background, the patient population being treated and recognized needs for improved treatments.

For dental implants manufacturing there are necessary to be realized in vitro tests of durability and biocompatibility, then preclinical investigations of implant configurations on large animals.

For investigation of bioactive materials/implants and combination and potentially tissue-engineered medical implants in which the interactions between the implant and the surrounding tissue are complex, research based on implant retrievial and evaluation continues to be critical.

A robust sterilization validation method embodies in national and international standards and they are the foundation for the strong patient safety record of terminal sterilizations.

Some biological materials may have undesirable responses to the techniques used and then may require special sterilization methods.

After prototype device have been designed and fabricated, biologic tests in vitro and in animals are normally used to gain more information for eventual regulatory approval and introduction of such an implant into clinic.

Many actual and future researches determine a development of different metallic alloys composition with very special properties like Ti-Ta alloy and Ti-Zr alloy.

REFERENCES

[1] D. R. Buddy, S. Hoffman, F. Schoen, and J. Lemons, *Biomaterials Science, An Introduction to Materials in Medicine*, 3rd ed, Academic Press, 2013.

[2] F. H. Silver and L. David, *Biomaterials Science and Biocompatibility*, Springer Verlag, 1999.

[3] B. P. Joon and J. D. Bronzi, *Biomaterials. Principles and Applications*, CRC Press, 1999.

[4] W. Schatt and K. P. Wieters, *Powder Metallurgy. Processing and Materials EPMA*, 1997.

[5] P. Berce, N. Balc, C. Caizar, R. Pacurar, A. S. Radu, S. Bratean, and I. Fodorean, *Tehnologii de fabricatie prin adaugare de material si aplicatiile lor*, Editura Academiei Romane, Bucharest, 2014.

[6] I. Vida-Simiti, *Technological Properties in Powders Metallurgy*, Editura Enciclopedică, Bucharest, 1999.

[7] A. F. von Recum, *Handbook of Biomaterials- Evaluation*, 2nd ed. 1999.

[8] H. V. Buf and G. Bușilă, "Technologies and Installation for Titanium Powder Manufacturing," in *Proc. Third Conference in Powder Metallurgy*, Cluj-Napoca, 1998, pp. 169-174.

[9] D. I. Băilă, O. C. Mocioiu, C. Zaharia, R. Trusca, A. Surdu, and M. Bunea, *Rev. Roum. Chim*, vol. 60, no. 9, pp. 921-930, 2015.

[10] D. I. Băilă, "Medical implants realized from the sintered compacts of titan-hydroxyapatite," *DAAAM Zadar Croatia*, pp. 594-596, 2013.

[11] D. I. Băilă, "Theoretical and experimental research on the assimilation of new biocompatible materials processed by RP (Rapid Prototyping) technology," Doctoral Thesis, Technical University of Cluj-Napoca, 2009.

[12] C. Rontescu, A. Pacioga, G. Iacobescu, and C. G. Amza, "Research on the mechanical properties of titanium biocompatible alloys obtained by sintering," *U.P.B. Sci. Bull., Series B*, vol. 78, iss. 2, pp. 195-202, 2016.

Băilă Diana Irinel is a lecturer in University Politehnica of Bucharest. She holds courses for the following subjects: manufacturing processes, manufacturing equipments.

She got the Ph.D in industrial engineering with thesis title "Theoretical and experimental research on the assimilation of new biocompatible materials processed by RP (rapid prototyping) technology" from Technical University of Cluj-Napoca, The Faculty of Machine Building in 2009. She is a member in 7 research contracts. Her 10 papers have been published in ISI journals with impact factor.