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PHYSICAL -MECHANICAL AND TECHNOLOGICAL CHARACTERISTICS OF Ti10Zr ALLOY FOR DENTAL APPLICATIONS

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ABSTRACT

Progress reported over time in dentistry can be attributed largely to the dynamics of acquiring new materials. A biomaterial is considered ideal in the absence of any biomaterial-tissue interaction, which means a biomaterial totally inert to the biological medium. Biomaterials currently used as implants that come in contact with the tissues and substances and fluids in the body must meet two basic characteristics, called bio-functionality and biocompatibility. They define both the ability to fulfill its function properly and the compatibility of the implant biomaterial with the tissue that it incorporates. The most common are metallic biomaterials (metals and alloys) due to their very good mechanical properties and their accepted biocompatibility. Issues related to the use of metallic materials in dental biomaterials (prostheses, implants) include mainly corrosion, release of toxic metal ions and wear. The toxicity of the metal ions as particles resulting from wear is a major disadvantage in the use of metallic biomaterials as they may induce multiple tissue reactions, such as osteolysis, damage the normal structure of the bone, severe reaction of macrophages, granuloma, fibrous capsule, inflammatory and immune reactions. All this can lead to implant destabilization and loosening.

This paper summarizes the physical-mechanical and technological characteristics of a new titanium-based alloy having high biocompatibility due to the chemical composition. The alloy is composed of 10% zirconium designed to improve fatigue strength in corrosive environment and does not contain harmful elements present in conventional titanium-based alloys composition.

KEYWORDS: biocompatibility implant, melting, cold crucible, casting, titanium-zirconium, microstructure

1. Introduction

In dentistry, metals and especially alloys have important broad applications, some are processed by casting in dental labs, other alloys are industrially cast and used such as implants, or after cold processing in laboratory for the manufacturing of the metal components of the various types of metal orthodontic appliances or partial movable acrylic dentures [1-4]. The term of Dental Metallurgy acquires new meanings through the modernization of the alloy making and processing techniques [5]. Dental alloys are part of a special class of biocompatible materials which, by their properties, should provide resistance to the phenomena specific to the oral environment. Of these, the most important is the corrosion process of the surfaces by biological, chemical, especially electrochemical action. Also, wear surfaces to form metal particles and release harmful metal ions that can migrate into tissues [6-10].

Dental alloys commonly used are: noble alloys (Au-Pt with 80% Pt), semi-noble alloys (Au-Pd with 50-60% Au), low noble alloys (Ag-Pd with 50-60% Pd) and not noble alloys (Ni-Cr with 75-85% Ni and 11-15% Cr; Co-Cr with 40-70% Co and 20-30% Cr; Fe-Cr with 59% Fe and 26% Cr; stainless steel with 18% Cr and 8% Ni, Co-Cr-Mo with 10-60% Co, 2-80% Ni and 10-30% Cr); Cu-Al alloys.

Generally, use is made of metals and alloys that are easily passivated. Although the passive oxide layer of such biomaterials remains intact, however, in the neighboring tissues, higher concentrations of metal ions occur which may affect the biomaterial-tissue interaction and can cause tissue damage over time. Stainless steel is very susceptible to salt corrosion environments, such as the tissue fluid. By corrosion, steel becomes a metal with low resistance to fatigue, the main cause of implant failure [10, 11]. Release of corrosion products (Ni^{2+}, Cr^{3+}, Cr^{6+}) causes inflammatory reactions. In endosseous implants, inflammation prevents osseointegration and favors the formation of a fibrous capsule [12-14].

Modern alloys based on Co-Cr, due to superior mechanical properties and advantageous cost price, have replaced noble alloys of class IV in the traditional (metal-polymer) and modern (metal and metal-ceramic composite) technology [4]. Chromium is the main alloying element that provides corrosion resistance and oxidation by forming oxide films (Cr_2O_3) adherent and continue that protect the surface. In dentistry, the cobalt-chromium-molybdenum alloys were used as subperiosteal implants, endosseous plates and transosseous implants.

Limiting the use of stainless steels only for temporary devices was called for by the appearance of superior titanium alloys ((Ti, Ti-Al-V, Ti-Ni, Ti-Al, Ti-Al-Nb) [15-17].

Although titanium is considered a biocompatible metal, Ti^{4+} ions inhibit in vitro the activity of osteoclasts and reduce osteoblasts protein synthesis; In a study using human osteoblast cell line MG-63, defined as proliferative osteoblast, Shida and his collaborators have shown that the Ti^{4+} ions induce the production of IL-6 and thus activates osteoclastogenesis.

Titanium alloy implants have significantly lower corrosion rates than those of other metallic implants, but they release metals in organism; Aluminum and Vanadium are elements released into the tissues. The metal ions released as a result of corrosion and wear process can induce denture loss after a long period of implantation, especially because of the potential adverse effects of vanadium. Release of vanadium ions in the body may cause serious diseases of breathing organs and the systems producing platelets [15-17].

For this reason, it is preferred the alloy of Ti-Al-Nb instead of Al-Ti-V [18-21]. In vitro studies have shown that cells behave differently in the presence of wear debris generated from the two alloys. Therefore, it is found an increased release of prostaglandin E2 in response to Ti-6Al-4V particles contact and an increase in the release of other inflammatory cytokines compared with Ti-Al-Nb particles. These data suggest that Ti-6Al-4V stimulate phagocytic cells more than the Ti-Al-Nb or pure Ti. Exposure of bone marrow cells derived from Ti-6Al-4V particles induces a significantly increased release of pro-inflammatory and osteolytic mediators which are responsible for the loss of denture [22].

It should be noted that the insertion of an implant lead to wound, and the healing success is closely related to the tissue response which depends, among other, on the surrounding tissue and the ability of the affected tissues to regenerate.

To summarize, in terms of materials and their effects, there are the following categories: materials with toxic response tissue (e.g. iron, nickel, cobalt, chromium, cadmium), materials that generate fibrous tissue (e.g. zinc, silver, aluminum, stainless steel, chrome - cobalt alloys), materials that induce vital reaction (e.g. titanium, ceramic, aluminum, zirconium ceramic).

Lately, in the dentistry world have appeared non-noble dental alloys complex allies helping to improve their specific properties, primarily their biocompatibility and the toxic effects of metals (Ni, Cr, Co, Ti, Al) released by the prosthetic implants are intensely studied.

2. Materials and experimental conditions

Titanium- based alloy (Ti10Zr) was developed in cold crucible furnace at R & D Consulting and Services SRL Bucharest. Magnetic levitation melting in cold crucible furnace applies to difficult fusible melted and very reactive metals such as titanium, niobium, tantalum, molybdenum, zirconium, etc. Given the alloy destination for medical applications, it is necessary to strictly comply with the quality of the metal materials used in its preparation. The chemical composition of the Ti10Zr alloy is shown in the Figure 1 and in the Table 1.

Table 1. *EDAX ZAF Quantification (Standard less), element normalized*

Elements	Wt. %	At. %	K-Ratio	Z	A	F
Ti-K	**87.72**	93.15	0.8271	1.0084	0.9350	1.0000
Zr-K	**12.28**	6.85	0.1111	0.9113	0.9933	1.0000
Total	100.00	100.00	-	-	-	-

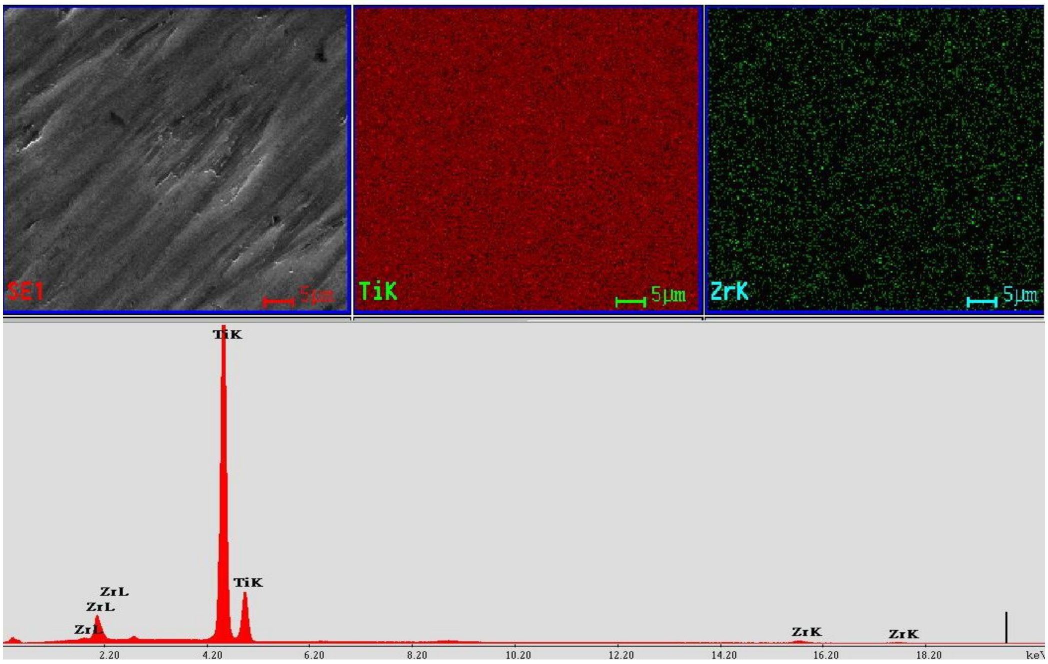
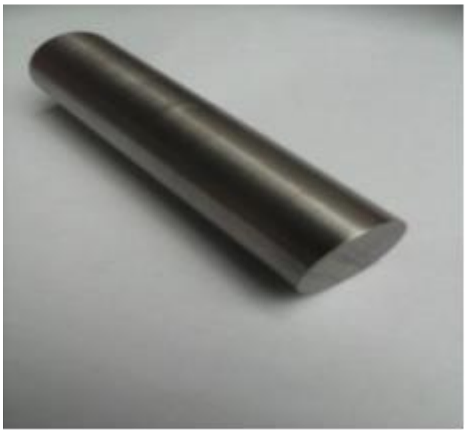


Fig. 1. *Scanning Electron Microscopy image (SEM) and EDX Spectrum of samples taken from Ti10Zr Alloy* Castings [5, 23-25]

3. Experimental results

Final ingots have a diameter of about 19 mm and length of 70 mm (Fig. 2). The implant was designed and made at SC TEHNOMED Bucharest (Fig. 1).


a

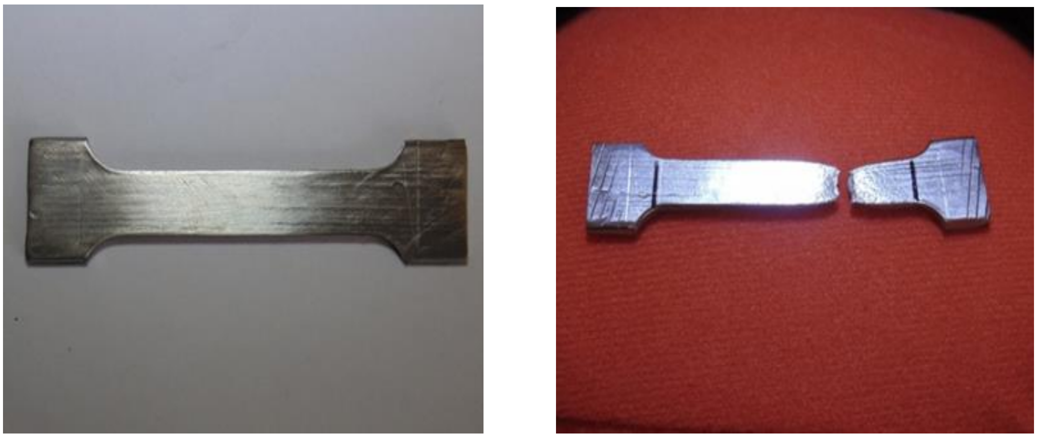

b

Fig. 2. *Cast alloy blank of Ti10Zr (ingot) (a) and dental implants (b)*

Knowing the behavior of the bio-alloy metallurgical processing (technical features) and under stress required analysis and laboratory tests, which evaluated the use potential of the alloy Ti10Zr as biomaterial for applications in dentistry.

In the following are presented the conditions for determining the mechanical characteristics of the alloy studied, in accordance with standards and regulations.

From initial ingot (Figure 1) were made standard samples (Figure 3), which were tested on the machine static axial tensile (Mechanical Testing Laboratory of AM Galati, Figure 3, Figure 4).



a b

Fig. 3. *Standard test specimen of alloy Ti10Zr tensile testing: before (a) and after the test (b)*

Fig. 4. *Tensile test machine to determine the mechanical properties of the alloy Ti10Zr (making the specimen from the initial blank and the tensile test)*

To study the behavior of the bio-alloy metallurgical processing by plastic deformation hot and cold, blank was processed initially by turning and subjected to heat to a temperature of 850 ºC. Heated preform was subjected to hot extrusion, the initial diameter of 10 mm then the Φ5 mm, followed by cold rolling to gauges respectively Φ4 mm diameter and Φ3 mm [23-25].

Research on structural changes and assessment of properties (micro-hardness) during processing (molding, extrusion 1 extrusion 2 cold rolling) described above were performed on samples cut from the blanks by milling undergo initial processing. Metallographic analysis shows a gradual finishing the structure and uniformity and homogenization of it [Fig. 6, Fig. 7].

Applied technology highlighted good deformation behavior of the alloy, a good plasticity and a trend of reduced hardening.

Processing by plastic deformation provides a fine structure and an increase of about 50% of the properties of hardness and strength [5]. In fact, the analysis carried out on fractographic bio-alloy samples, and the test results of tensile test (the study of the fracture surface at different magnifications Figure 8) show a ductile fracture, the investigated fracture surface being clean and free of cracks and inclusions, without confirming good behavior of the hot and cold plastic deformation processing of the bio-alloy.

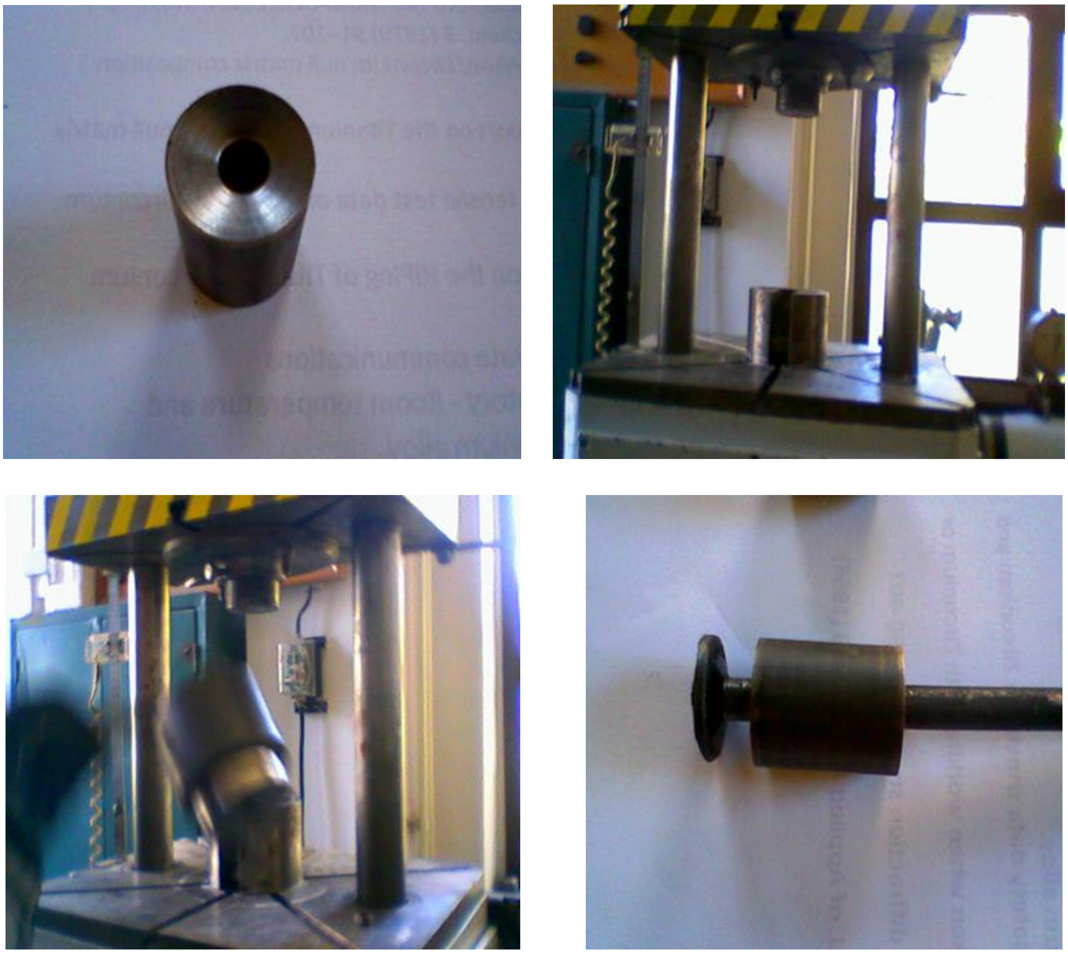


Fig. 5. *Aspects of the stages of hot extrusion molding to a diameter of 10 mm of the blank having 18 mm diameter and 35 mm length; the new blank of Φ10x35 mm was subject to heating at 850 °C then hot extruded at the Φ5 mm diameter. Finally, the Φ5 mm extruded blank was cold rolled to a diameter of Φ3 mm*

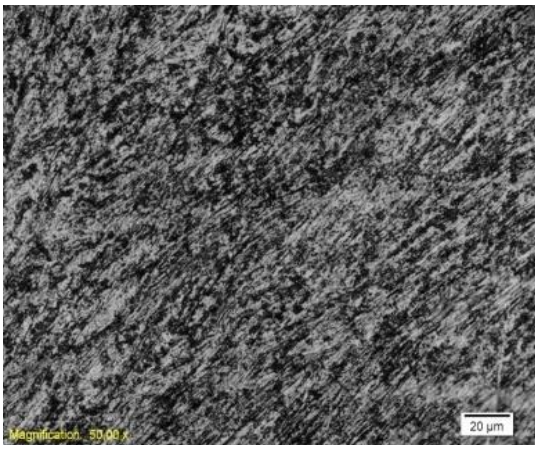


Fig. 6. *Microstructural aspects condition: extruded from Φ10 mm to Φ5 mm* [23-25]

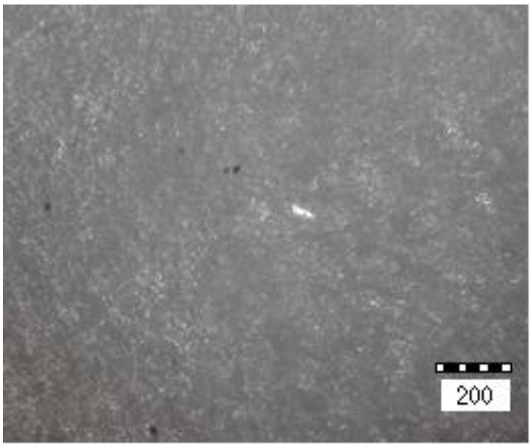
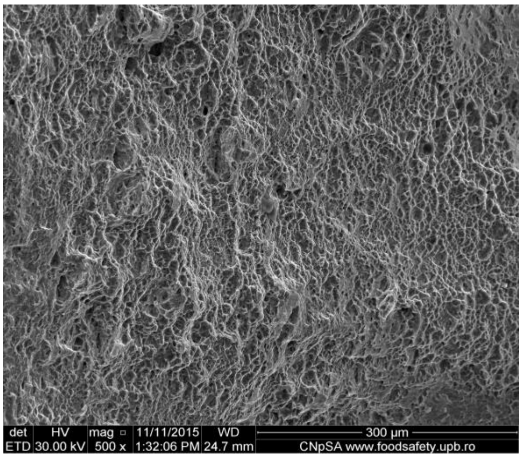
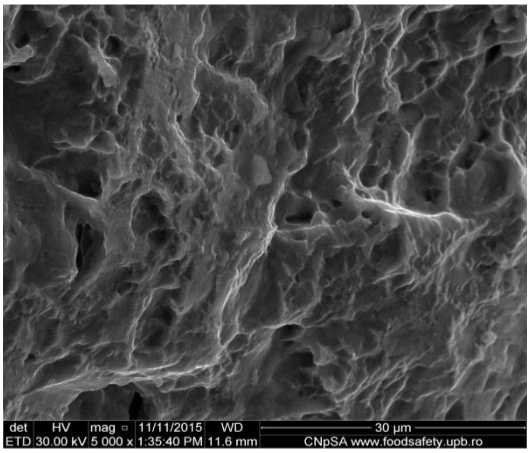


Fig. 7. *Microstructural aspects (optical microscopy, structural condition – cold rolled: a.) to d = 4 mm; b.) to d = 3 mm* [5]



X500



X5000

Fig. 8. *Characteristics of ductile fracture samples from the bio-alloy Ti10Zr (SEM analysis at different magnifications)* [5]

3.1. Determination of Young's modulus and hardness using the micro-indentation [5]

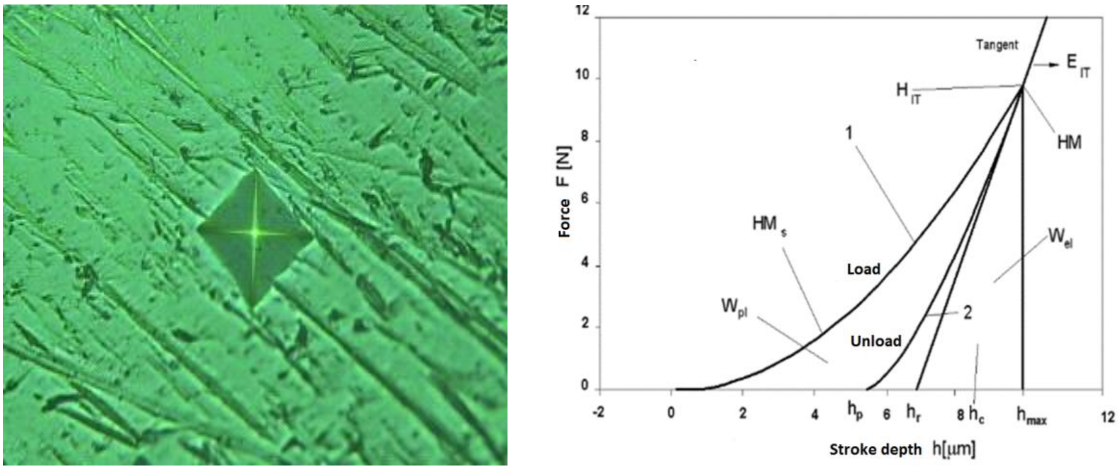
Experimental alloys studied were tested for hardness and elastic modulus determination. We used a hardness tester for determining hardness on the principle Martens, ultra-micro-hardness testing device DUH-211S Shimadzu from Laboratory Testing and Material Characterization of the Faculty of Food Engineering of the University "Stefan cel Mare" Suceava.

3.2. Universal Hardness test - HU

Compared to the conventional method of testing for hardness (Brinell, Vickers and Rockwell) in which the values specific to deformation is determined only after removal of the load, i.e. the calculation of the hardness is only used for part of the plastic universal deformation hardness test (HU), and the size of specific deformation under load is determined. Also, the universal hardness is used for the calculation of the component as plastic deformation as well as elastic deformation component. The test was carried out under loading and unloading the progressive indenter reading, and memorizing pairs of values: force (F) - depth of penetration; (h) offers the possibility of determining not only the hardness HU, but also of important mechanical characteristic units such as: modulus of elasticity, which is elastic deformation, tend to creep tendency seating capacity of hardening of the material, etc. [documentation on testing conditions was carried out in the Laboratory of testing and material characterization at the University "Stefan cel Mare" Suceava]. During the test, load is measured both at discharge and at pairs value force (F) and depth of penetration (h).

Table 2. *Mechanical characteristics of the samples from Ti10Yr bio-alloy (Shimadzu DUH 211S)* [5]

Sample Type	**F_{max}**	**h_{max}**	**HMV**	**HM_s**	**H_{it}**	**E_{it}**	**C_{it}**	**n_{it}**	**HV***	**HV**
Ti10Zr	[mN]	[µm]	[N/mm²]	[N/mm²]	[N/mm²]	[N/mm²]	[%]	[%]		
	1000	48.794	1599.956	998.015	2054.839	7.574e+004	1.623	17.863	194.18	228.36
		49.369	1563.539	1052.730	1968.489	8.091e+004	1.759	16.855	186.02	214.47
		49.393	1562.355	1188.072	1992.908	7.604e+004*	1.588	17.796	188.33	221.51
Average value		**49.185**	**1575.283**	**1079.606**	**2005.412**	**78325**	**1.656**	**17.504**	**189.51**	**221.44**



a b

Fig. 9. *Footprint indenter (The impression) on the sample alloy Ti10Zr (a), the graphic representation of the evolution of pairs of values, force (F) - penetration depth (h) (b), if the charging process (1) - Download (2) to test the hardness Martens* [5]

The experimental results are presented regarding the measured characteristic parameters for Ti10Zr alloy hardness testing, using the Shimadzu DUH-211S device.

4. Conclusions

The analysis of physico-chemical and technological characteristics of the new alloy (Ti10Zr) with high biocompatibility in terms of composition (chemical elements such as vanadium and aluminum were removed etc.) shows the following:

a. comparable physical and mechanical properties of titanium alloys commonly used in dental applications respectively:

- low density (4.7 g / cm^3), comparable to pure titanium (4.51 g / cm^3) and conventional titanium alloys;

- relatively low modulus of elasticity (E = 94.2 - 113 GPa, depending on the method of determination);

- mechanical characteristics: Rm = 636 MPa, Rc = 527 MPa, A = 31.2%.

b. metallurgical hot and cold processing of the Ti10Zr alloy showed good deformation behavior of the alloy, good plasticity (an increase of about 50% of hardness and resistance) and reduced hardening tendency.

References

[1]. Kenneth J., *D.M.D. Anusavice*, Phillips’ Science of Dental Materials, Tenth Edition, 1996.

[2]. Park J. B., *et al.*, *Biomaterials, Principles and Applications*, MA: CRC Press, 2003.

[3]. Craig R. G., *Materiale dentare restaurative*, Ed. All Educational, Bucuresti, p. 22, 2001.

[4]. Vasilescu E., *Research on the Behaviour of the Tooth- Crowns Assembly Made of Different Materials in Solutions simulating the Oral Environment*, The Annals of "Dunarea de Jos" University of Galati Fascicle lX. Metallurgy and Materials Science, no. 3, p. 27, 2015.

[5]. Vasilescu V. G., *Contribuţii la studiul materialelor metalice biocompatibile utilizate în implantologia orală*, Teză de doctorat susţinută la U.M.F. “Carol Davila“ Bucureşti, 2016.

[6]. Anderson J. M., *et al.*, *Host reactions to biomaterials and their evaluation*, Ratner B. D., *et al.*, eds. Biomaterials Science: An Introduction to Materials in Medicine London, Elsevier, 2004.

[7]. Khan M. A., Williams R. L., Williams D. F., *In vitro corrosion and wear of titanium alloys in the biological environment*, Biomaterials, 17, p. 2117, 1996.

[8]. Patrascu I., Vasilescu E., Gatin E., Cara-Ilici R. R., *Corrosion of Biomaterials Used in Dental Reconstruction Dentistry*, Chapter 26, 2014.

[9]. Patrascu I., Vasilescu V. G., Milicescu St., *Modern methods for assessing the corrosion resistance of dental alloys used in dentistry*, Chapter 9, 2014.

[10]. Gadea S., Petrescu M., *Metalurgie fizica si studiul metalelor*, vol. 3, EDP Bucuresti, 1983.

[11]. Ghiban B., *Metallic Biomaterials*, Editura Printech, Bucuresti, 1999.

[12]. Fleck C., Eifler D., *Corrosion, fatigue and corrosion fatigue behaviour of., metal implant materials, especially titanium alloys,* International Journal of Fatigue, 32, p. 929-935, 2010.

[13]. Montes C. C., Pereira F. A., Thome G., Alves E. D. M., Acedo R. V., Renato de Souza J., Moreira Melo A. C., Trevilatto P. C., *Osseointegrated Dental Implant Loss.*, Implant Dentistry, vol. 16, no. 4, 2007.

[14]. Hadi S. A., Ashfaq N., Bey A., Khan S., *Biological factors responsible failure of osseointegration in oral implants*, Biology and Medicine, 3 (2), Special Issue, p. 164-170, 2011.

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

[16]. Imam M. A., Fraker A. C., *Titanium alloys as implant materials*, In: Brown SA, American Society for Testing and Materials, p. 3-16, 1996.

[17]. Vlad Gabriel Vasilescu, Elisabeta Vasilescu, *Consideraţii asupra compoziţiei aliajelor cu baza titan utilizate in implantologia orala*, Congresul National GALMED, Editia a-V-a, 13-16 noiembrie 2014 Galati Romania (volum de abstracte/prezentare poster).

[18]. Moranta C., Lopez M. F., Gutierrez A., Jimenez J. A., *AFM and SEM Characterization of non-toxic vanadium-free Ti alloys used as biomaterials*, Applied Surface Science 220 Elsevier, p. 79-87, 2003.

[19]. Okazaki Y., Gotoh E., *Comparison of metal release from various metallic biomaterials in vitro*, Biomaterials, 26, 11, 2005.

[20]. Khan M., Williams R., Williams D., *The corrosion behaviour of Ti–6Al–4V, Ti–6Al–7Nb and Ti–13Nb–13Zr in protein solutions*, Biomaterials, 20 (7), p. 631-637, 1999.

[21]. Drăgan (Raileanu) L. A., Petreus T., Tudoran L. B., Munteanu C., Mareci D., Cotrutz C. E., Chelariu R., *Cytocompatibility evaluation of two new Ti-Nb-Zr-Al alloys for medical applications*, Elsevier Editorial System(tm) for Materials Science and Engineering C.

[22]. Campos M. I., Godoy dos Santos, Leme M. S., Trevilatto P. C., *Interleukin-2 and Interleukin-6 gene promoter polymorphisms, and early failure of dental implants*, Implant Dentistry, vol. 14(4), p. 391-398, 2005.

[23]. Vasilescu V. G., Patrascu I., Cotruț C., Vasilescu E., *Experimental Research on the Behavior of the Alloy Ti10Zr in Simulated Oral Environment*, Rev. Chim. (Bucharest), no. 2, p. 263, 2016.

[24]. Dima O., Alexandru P., Gurău G., Vlad Gabriel Vasilescu, Elisabeta Vasilescu, *Studies and Research on Treatment of Titanium Alloys*, UgalMat 2014, Galati, The Annals of "Dunarea de Jos" University of Galati. Fascicle IX. Metallurgy and Materials Science no. 1, 2014.

[25]. Vasilescu Vlad Gabriel, Patrascu Ion., Vasilescu Elisabeta, *Studies and Research Regarding the Influence of Metallurgical Processing on the Structure and Properties of* some *Titanium Based Alloys Used in Dentistry*, The VIth Edition of International Conference UgalMat 2014, Advanced Technologies and Material Section, May 29-31, Dunărea de Jos" University of Galati, Romania, 2014.

[26]. Vlad Gabriel Vasilescu, Elisabeta Vasilescu, *Aliaj Ti-Zr utilizat in implantologia orala*, Congresul National cu participare internationala pentru studenti si tineri medici rezidenti, GALMED Editia a V-a, 13-16 noiembrie 2014, Galati, Romania (volum de abstracte/prezentare poster).