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Chapter

Development of New Advanced Ti-Mo Alloys for Medical Applications

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Abstract

The use of titanium and titanium-based alloys with applications in implantology and dentistry has made remarkable progress in the promotion of new technologies and new materials that have been developed in recent years. This is justified thanks to their excellent mechanical, physical, and biological performance. Today's generation promotes new titanium alloys, with nontoxic elements and long-term performance and without rejection of the human body. This book chapter describes new original compositions of Ti-based alloys for medical applications, with improved properties compared to existing classical alloys (C.p. Ti, Ti6Al4V, CoCrMo, etc.). The addition of nontoxic elements such as Mo, Si, Zr, and Ta brings benefits as reduced modulus of elasticity, increased corrosion resistance, and improved biocompatibility.

Keywords: Ti-Mo alloys, microstructural characterization, corrosion resistance, low elastic modulus

1. Introduction

Materials with the possibility of performing a biological function are increasingly sought. In the medical field, implants require a high compatibility with the hard tissue for osteointegration and bone formation and a compatibility with the soft tissue for the adhesion of the epithelium to them and the acquisition of anti-bacterial properties for inhibiting or forming the biofilm at the interface. These biofunctional characteristics have two contradictory properties: inhibition and enhancement of protein adsorption, respectively, and cell adhesion [1, 2].

The usual classification of synthetic biomaterials is carried out structurally, according to the classes of materials used. The main types of synthetic biomaterials are metallic, ceramic, polymeric, composite, and of natural origin, but they can also be divided into several categories, as can be seen in **Figure 1**.

Biocompatible materials are intended to "work under biological constraint" and thereby become adapted to various medical applications.

When a metallic material is implanted in a human body, immediate reactions occur between their surface and the living tissues. In other words, an immediate reaction during the introduction period is determined and defines the biofunctionality of the metallic material [3].

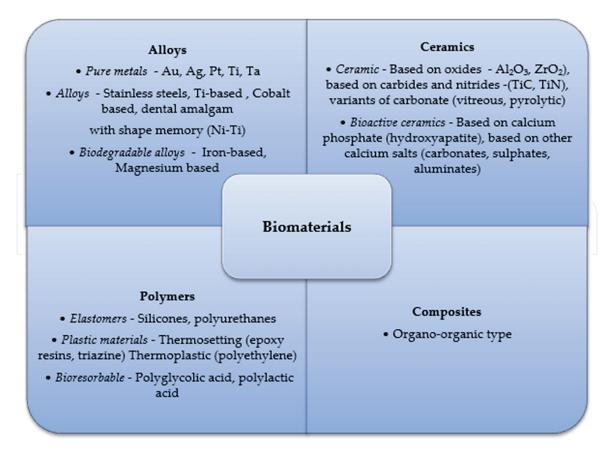


Figure 1.
The main types of biomaterials [4].

The quality of a material used in the construction of an implant must respect the following two criteria: the biochemical criterion and the biomechanical criterion. According to the biochemical criterion, the applicability of a material is determined by its biocompatibility, and from the biomechanical point of view of fatigue resistance, it is the most important parameter but not the only one.

The most used metallic biomaterials are stainless steels, Co-Cr alloys, titanium alloys, and magnesium-based alloys. Each class of biomaterials has its advantages and disadvantages (**Figure 2**), their use in the execution of different implants being influenced by both the properties of the biomaterials and the functional requirements imposed to the implants [5].

Among the most important factors that intervene on a biomaterial successfully integrated in the human body, we mention the physical-chemical properties, the design, the biocompatibility, the surgical technique applied to the implantation, and last but not least, the patient's health.

The selection of materials used in contact with living cells or tissues for implantation in the human body, as biomaterials, is determined primarily by their acceptance by the human tissues with which they interact (biocompatibility) and by the ability to perform their functional role for which they were implanted (biofunctionality) [6].

Out of the metallic biomaterials, a special interest is for those with osteotropic structure, of which the titanium belongs. These biomaterials, thanks to the chemical and micromorphological biocompatibility with the bone tissue, achieve with this physical-chemical connection, the interface phenomenon being assimilated with the linking osteogenesis.

Titanium alloys are frequently used, due to the need of replacing stainless steels and cobalt-based alloys that have limitations in use, causing some deficiencies of biocompatibility with human tissues. These deficiencies are caused by some elements present in their chemical composition (e.g., nickel), which have a toxic effect

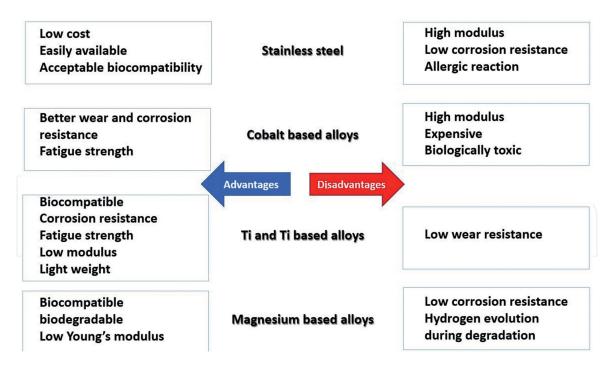


Figure 2.Main characteristics of metallic orthopedic implants [6].

on human tissues, causing inflammatory allergic reactions or implant rejection reactions [7].

The properties of the titanium are as follows:

- melting point—the titanium melts at 1660°, and it can be sterilized without risk at 300°;
- resistance—the implants are made from a single pure titanium bar by mechanical processing, giving them maximum resistance;
- hardness—the titanium has a hardness comparable to that of steel, giving it special mechanical quality;
- rigidity—the implants do not deform when applying, mounting, or milling forces nor in the biomechanics of chewing;
- nonmagnetic—the titanium has no magnetic effect, resulting in good tissue supportability;
- regenerative and therapeutic action—research and practical experience have highlighted the healing qualities of titanium oxide;
- neutral pH—titanium dioxide, TiO₂, which is formed immediately around the metal molecules, has a pH of 7, completely neutral;
- biological immunity—the implant can be stimulated in contact with the bone, surrounding tissues and the oral cavity environment;
- excellent resistance to electric shock—the titanium has a very low thermal conductivity; and
- light weight—the density of titanium is close to that of light alloys [4, 8].

The biocompatibility of titanium is a consequence of the presence of the superficial oxide layer. The chemical properties and therefore the chemical processes on the interface are determined precisely by this layer of oxide and not by the metal itself. This feature is applicable to all metal materials used in the manufacturing of implants and prosthetic parts. Among the metal materials used for hard tissue repair in human body, the elastic modulus of titanium (about 80–110 GPa) is the closest to hard human tissue, which can reduce the mechanical incompatibility between metal implants and bone tissue [9].

Titanium alloys are used for medical applications in multiple fields in human body and became the first choice for orthopedic products. **Figure 3** shows the main applications of titanium alloys used in orthopedic applications [2–8].

In conclusion, it can be said that titanium biomaterials, by its properties, respond to almost all the requirements necessary for the achievement of osteogenesis, osteointegration, and durability over time. The pure titanium implant offers perfect compatibility, correct and concrete osteogenesis, and demonstrable timelapse viability.

Adding the alloying elements gives titanium a wide range of properties through different microstructures and properties.

After microstructure, the alloys are grouped into three categories depending on the type of stabilizing elements added to the titanium alloy. The mechanical properties and corrosion resistance of the alloys depend on the morphology and structure of the α or β phase particles in the alloy matrix.

Thus, the alloying elements are divided into three categories as follows:

- α stabilizers: C, N₂, O₂, and Al;
- β stabilizers: V, Nb, Mo, Ta, Fe, Mn, Cr, Co, W, Ni, Cu, Si, and H₂; and
- neutral elements: Zr, Sn, Hf, Ge, and Th [1, 5, 8].

Over the years, many titanium alloys have been developed and investigated for the implantation of implants for medical applications, of which few have been accepted by the human body, namely those that have certain properties necessary for long-term success.

The biocompatibility of an alloy depends on the alloying elements. Alloying elements such as Zr, Ta, Nb, and Sn do not affect cell viability and have shown a reduced amount of ions released into the body, but Al and V contribute to reducing cell viability. Other elements such as Ag, Co, Cr, and Cu have moderate cytotoxic behavior, but their presence in these alloys significantly reduces their toxicity [1–5]. By analyzing the current research, these alloys were studied in order to develop

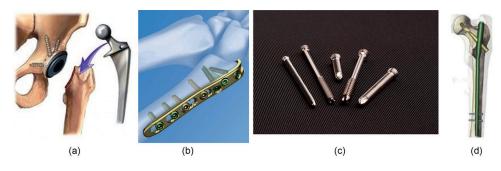


Figure 3.Orthopedic products made by titanium and titanium alloys: (a) endoprosthesis for joint replacement; (b) system plate screws for bone fracture repair; (c) screws for bone repair; and (d) intramedullary nail [2, 9].

new recipes of titanium-based alloys with elements with high biocompatibility on human tissue such as Mo, Ta, Zr, and Si [10, 11].

2. Characterization of the obtained titanium alloys

The experimental tests aim at a characterization of new developed titanium alloys by chemical, structural, surface, and mechanical analyses.

This chapter describes the following investigations for the new alloys developed:

- **Development of alloys** was carried out using a Vacuum Arc Remelting installation for the elaboration of homogeneous alloys.
- **Elemental composition** is necessary to determine the percentages of the chemical elements that make up the elaborated titanium alloys.
- **Structural characterization** is necessary for the study of the microstructure, the crystallographic orientation, the texture, and the identification of the constituent phases.
- **Mechanical characterization** highlights the mechanical properties of the developed titanium alloys: hardness and elasticity module.
- **Corrosion resistance** determines the stability of the proposed alloys in the simulated body fluids.
- Surface characterization takes into account the measurement of the contact angle of the surface of the alloys for achieving/optimizing the adhesion and cell proliferation.

2.1 Vacuum arc remelting

In order to obtain the titanium alloys, the MRF ABJ 900 Vacuum Arc Remelting has been used. Vacuum arc remelting is a commonly used process in the development of alloys. The process itself is used to refill the ingots and refine the structure by using nonconsumable mobile electrode of thorium tungsten. The process itself can also be used to obtain special alloys, superalloys, and titanium alloys.

In principle, the process of remelting with a vacuum arc is a process based on continuous melting with the use of the electric arc and nonconsumable mobile electrode.

Advantages of using this equipment are as follows:

- It can achieve very high melting temperatures.
- It ensures the possibility of melting the metallic vacuum samples under a protective atmosphere by means of a nonconsumable mobile electrode of thorium tungsten.
- It creates alloys with uniform composition, through repeated remeltings.
- It ensures the possibility of mixing elements with different melting temperatures.

- It can use various crucibles for elaboration and ensure the possibility of obtaining the samples under specific conditions in the form of a pill of different shapes and sizes.
- Loading and unloading is done in a simple way by lifting the cover that is caught in the hinge to the rest of the camera.
- It is illuminated with a halogen lamp, thus helping to control the melting of the alloying elements in the process [12].

Figure 4 shows all stages of titanium alloying, which includes the weighing of the raw material, the loading of the alloying elements, and the final semi-finished obtained products.

The load calculation has considered the characteristics of the different alloying elements and their physical-chemical properties.

Elaboration of the alloys was carried out in two charges to obtain two alloys in each charge. **Table 1** shows alloys proposed the cavities used for each alloy.

Elaboration of the titanium alloys made with a vacuum arc melting system, took place by the melting of the elements, and followed by the remeltings of alloys for six times, a necessary operation for the refining and homogenization of the alloys. The melting of the elements took place uniformly, resulting alloys with a precise and homogeneous chemical composition. The samples had a homogeneous structure, which means that the installation, the elaboration protocol, and the elements were chosen correctly.

After the solidification, two samples of each alloy were obtained in the form of ingots, shapes, and different masses but with sufficient quantity for taking the specimens required for all proposed laboratory tests.

2.2 Determination of the chemical composition of titanium alloys by EDAX analysis

A complete characterization of a metallic material consists in knowing its composition, the concentration of the various elements, or the impurities in the mass of the alloy. An extremely important aspect is the determination as precisely as possible of the chemical composition of the titanium alloys obtained after elaboration.

The EDAX system is a microanalysis detector, equipped with an electron microscope, which uses the resulting X-ray energy on the surface of the samples.

Determination of chemical composition can be performed, both punctually and in a well-defined region on the surface of the analyzed sample.

This method is a variant of X-ray fluorescence spectroscopy, in which the sample investigation is based on the interactions between the electromagnetic radiation and the sample, analyzing the X radiation emitted by the sample as a response to the charging of particles loaded with electric charges. The characterization possibilities are largely according to the fundamental principle that each chemical element has a unique atomic structure that allows the characteristic X-rays of the atomic structure of an element to characterize it uniquely from another.

In order to achieve the structural and thermal characterization, it is necessary to identify the chemical composition of the alloys obtained. EDAX microanalysis with energy dispersion of X radiation was used to determine the chemical composition of the TiMo alloys developed. Determination of the chemical composition by EDAX microanalysis is the first laboratory investigation required to highlight the proportions obtained between the pure chemical elements and was performed on titanium alloys obtained.



Figure 4.Stages of titanium alloying obtaining process: (a) weighing of raw materials and gravimetric dosing; (b) loading of the raw material; and (c) titanium semi-products obtained after solidification [12].

Alloy element	Ti	Mo	Si	Zr	Ta
			(% weight)		
Ti15Mo0.5Si	84.50	15.00	0.50	_	_
Ti20Mo0.5Si	79.50	20.00	0.50	_	_
Ti15Mo7Zr10Ta	68.00	15.00	_	7.00	10.00
Ti20Mo7Zr10Ta	63.00	20.00	_	7.00	10.00

Table 1.Chemical composition proposed of the new titanium alloys.

In order to validate the results regarding the concentration, for each sample, 10 measurements on five different areas were done.

To determine the chemical composition of the obtained titanium alloys, the Vega Tescan LMH II equipment was performed using the EDAX by Bruker attached to the SEM equipment.

For the determination of the chemical composition of alloys obtained from the TiMo system, samples having dimensions of $10 \text{ mm} \times 10 \text{ mm} \times 5 \text{ mm}$ were used. Before being examined, the samples were ground on abrasive paper to remove impurities and titanium oxide film on the surface of the alloy.

Table 2 shows the mass percentages of the elements identified in the alloy composition, the percentages of the elements varying slightly with the theoretical batch calculation.

Figures 5–8 highlight EDX spectrum and element mapping of titanium alloys.

Alloy element	Ti	Mo	Si	Zr	Ta
			(% weight)		
Ti15Mo0.5Si	79.28	19.95	0.77	_	_
Ti20Mo0.5Si	78.98	20.06	0.96	_	_
Ti15Mo7Zr10Ta	75.40	10.41	_	7.69	6.50
Ti20Mo7Zr10Ta	71.51	14.05	_	7.04	7.40

 Table 2.

 Chemical compositions of titanium alloys, expressed as a mass percentage, according to the EDX measurements.

The analysis of the chemical composition obtained revealed that the main elements identified in the alloys elaborated are Ti, Mo, Zr, Ta, and Si, without the presence of other inclusions.

2.3 Structural characterization of titanium alloys by optical microscopy

Microscopic methods of structural analysis are used to characterize the materials based on their structure, constituents and phases present (nature, shape, dimensions, and distribution), and possible structural defects (pores, cracks, structural inhomogeneities, etc.). Structural analysis was performed using the OPTIKA XDS-3 MET microscope.

In order to investigate the metallographic structure, the preparation of the metallographic samples of the experimental titanium alloys included a sequence of steps: cutting to appropriate dimensions (e.g., $10~\text{mm}\times10~\text{mm}\times5~\text{mm}$), incorporation in epoxy resin, grinding and polishing, and chemical attack with specific reagents (a solution with 10~mL of HF, 5~mL of HNO₃, and 85~mL of H₂O) for 30~s. After the preparation of the samples, this was analyzed at the optical microscope at various magnification powers in order to obtain detailed images on the microstructure.

Figure 9 highlights images obtained by optical microscopy for titanium alloys at $100 \times \text{magnification}$.

In **Figure 9**, the structure of titanium alloys with aspects of the specific grains of titanium is presented. The images obtained by optical microscopy for the elaborated alloys show a dendritic structure with irregular grain boundaries. These coarse structures are specific to β alloys.

The variation of the α , $\alpha + \beta$, and β type phases consists of the differences in chemical composition of the constituent elements. The high percentage of β -stabilizing elements (Mo, Ta, and Si) led to the formation of a β -type structure, very well highlighted in the elaborated TiMo alloys.

2.4 Mechanical characterization

2.4.1 Microindentation method

The measurement of the longitudinal elastic modulus for the obtained titanium alloys was achieved by the microindentation method. This method consists of penetrating the surface of the sample with a conical palpate at a certain force.

From a practical point of view, the indentation characterization presents a major advantage over the standard methods of testing on standardized tests, namely, the testing can be done directly on the finished pieces.

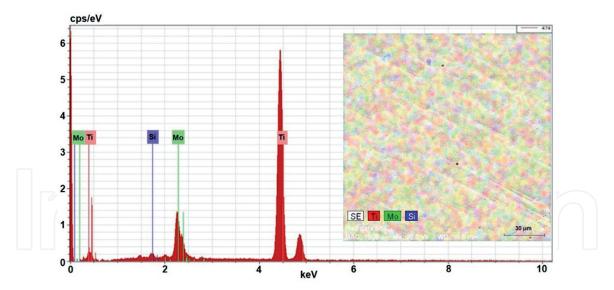


Figure 5. EDX spectrum and mapping for Ti15M00.50Si alloy.

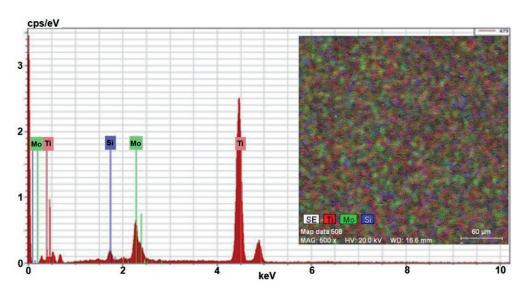


Figure 6. EDX spectrum and mapping for Ti20Mo0.50Si alloy.

During the microindentation test, the values of the loading forces are recorded relative to the penetration depth of the indenter in the material. Based on the loading-unloading curve, a number of sizes can be determined that allow the characterization of the materials.

Figure 10 shows the response of the alloys during the indentation tests in the form of force-depth dependencies. The values of the modulus of elasticity for the titanium alloys resulting from the indentation test are shown in **Table 3**.

Among the mechanical properties that are considered when evaluating a biomaterial is the longitudinal elasticity module. If the biomaterial is used for orthopedic implants, it must have a modulus of longitudinal elasticity equivalent to that of the bone, which varies between 4 and 30 GPa, depending on the type of bone and the direction of measurement [13–15].

A low modulus is reliable in inhibiting the bone resorption and enhancing the remodeling of bones, which may be due to the excellent stress transmission between the bone and the implant. A biomedical orthopedic implant should have a Young modulus matching or closer to that of human bone to avoid the stress shielding effect.

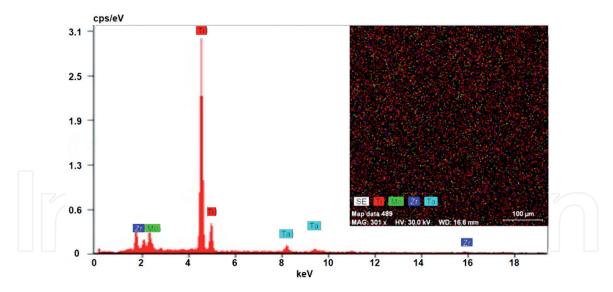


Figure 7. EDX spectrum and mapping for Ti15Mo7Zr10Ta alloy.

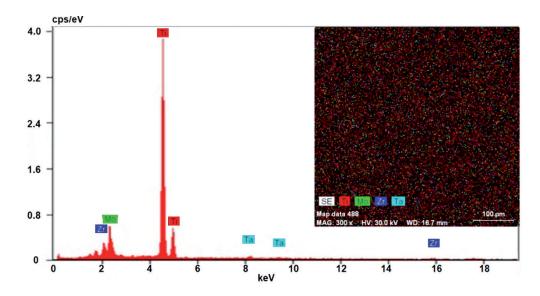


Figure 8. EDX spectrum and mapping for Ti20M07Zr10Ta alloy.

The developed titanium alloys have a low modulus of elasticity, close to that of the bone, with the exception of the Ti15Mo7Zr10Ta alloy and significantly lower values than CoCr alloys.

If the balance between mechanical properties and biocompatibility is achieved by both the implant and the bone tissue, the risk of negative effects is very small. The use of titanium materials with a low modulus of elasticity seems to be a good solution, and the chances of using the material for medical purposes are increasing.

2.4.2 Determination of hardness for titanium alloys

Hardness is a property of materials that express their ability to resist the action of mechanically penetrating a tougher body into its surface. When determining the hardness of the materials, the size of the traces produced by a penetration body, characterized by a certain shape and size, and the force acting on it is taken into account.

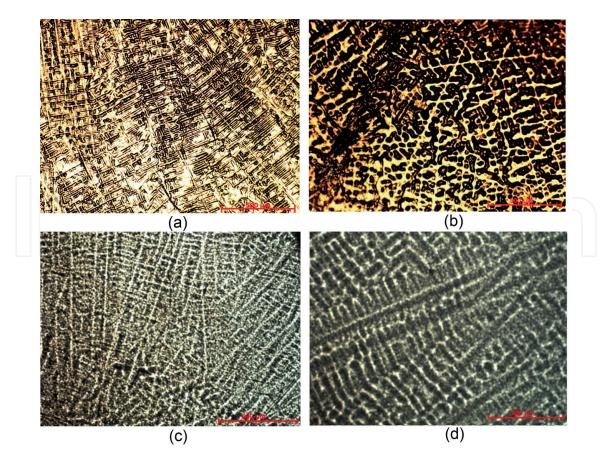


Figure 9.Optical microstructure of alloys investigated at 100× magnification power: (a) Ti15M00.5Si, (b) Ti20M00.5Si, (c) Ti15M07Zr10Ta, and (d) Ti20M07Zr10Ta.

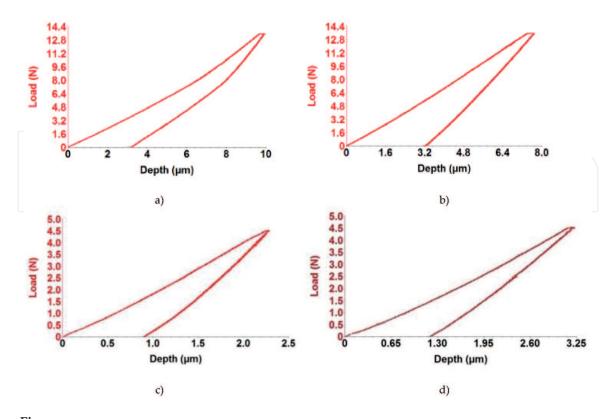


Figure 10.
The force-depth curve of the micro-indentation test for the investigated alloys: (a) Ti15M00.5Si, (b) Ti20M00.5Si, (c) Ti15M07Zr10Ta, and (d) Ti20M07Zr10Ta.

Alloy	Ti15Mo0.5Si	Ti20Mo0.5Si	Ti15Mo7Zr10Ta	Ti20Mo7Zr10Ta	C.p. Ti	Ti6Al4V	CoCr alloys	Human bone
Elastic modulus (GPa)	19.81	37.53	76.88	43.41	105	110	240	17
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The bold values represent the values of the classical alloys used in implantology, values that do not belong to us and are for a comparative points. They were bold to see the good results of our alloys.

Table 3. Elastic modulus values for titanium alloys measured by indentation test [13, 14, 16, 17].

The methods for determining the hardness, depending on the speed of the force on the penetrator, are classified into static methods, where the drive speed is below 1 mm/s, and dynamic methods for which the drive speed exceeds this value.

The Vickers hardness determination method uses a diamond penetrator in the form of a pyramid with a square base and consists in pressing it at a reduced speed and with a certain predetermined force F on the surface of the test material. The Vickers hardness, symbolized by HV, is expressed by the ratio of the applied force F to the area of the lateral surface of the residual trace produced by the penetrator. The trace is considered to be a straight pyramid with a square base, with diagonal d, having the same angle as the penetrator at the top.

For the Vickers hardness determination method, at least three attempts are made on the test material. For each trace, the average diagonal value is calculated based on the magnitude of the two diagonals measured. It is recognized that the difference in diagonal dimensions is within an error margin of not more than 2%.

The hardness measurements highlight resistance and provide information on the behavior of the studied materials. In this way, we can analyze titanium alloys developed for the purpose of fitting them into a specific medical application (**Table 4**).

HV hardness measurements on titanium alloys were performed with Wilson Wolpert 751N.

Both systems studied have different hardness results. Compared to other titanium biomaterials, TMZT alloys have a higher hardness, but close to the Ti6Al4V alloy, which are most commonly used in implantology. An important aspect that might have contributed to the increased hardness is the amount of stabilizing β elements. It can be observed that as the amount of stabilizing β elements increases (Mo and Ta), it decreases the hardness values.

2.5 Corrosion resistance

Corrosion represents the physical-chemical, spontaneous, reversible, and undesirable destruction of metals and alloys under the chemical, electrochemical, or biological action of the environment.

Corrosion monitoring is the practice of qualitative assessment and quantitative measurement of the corrosivity of an environment on a metal or an alloy immersed in this environment. Monitoring tests can be performed using mechanical, electrical, electrochemical, or chemical methods [18–20]. The nature of the monitoring sensor depends on the technique chosen for the study, the purpose pursued, and the particular characteristics of the sample used. In the older methods, the electrical measurements were often used, the monitoring technique and the methods of processing the experimental data being generally very laborious. The advances in the field of microelectronics have allowed the signals of the electrochemical sensors to be strictly conditioned, appropriately amplified, and processed based on complex data processing programs.

Some techniques and methods of measurement allow continuous monitoring of corrosion—the sample is permanently exposed in the corrosion environment, while the discontinuous methods are done only in specialized laboratories.

Alloy	Ti15Mo0.5Si	Ti20Mo0.5Si	Ti15Mo7Zr10Ta	Ti20Mo7Zr10Ta	C.P. Ti	Ti6Al4V	CoCr alloys
HV	233.37	165.18	462.33	321.31	128	381	600

The bold values represent the values of the classical alloys used in implantology, values that do not belong to us and are for a comparative points. They were bold to see the good results of our alloys.

Table 4.The hardness values of titanium alloys measured by the Vickers method [5, 13, 14].

Some techniques give direct information on material degradation or corrosion rate, while others are used to determine if a corrosive environment may exist. Also, some techniques are "destructive" altering more or less the surface of the metal, while others are nondestructive. The true methods of monitoring the corrosion are considered very sensitive measurements, which give a practical instantaneous signal, simultaneously with the change of the corrosion speed.

To obtain a more complete picture of the corrosion process, it is often necessary to obtain complementary data, from other sources or sensors, which are purchased simultaneously with those obtained from the corrosion sensor.

Three main aspects are pursued in the study of corrosion of alloys in various environments: (1) the type of corrosion involved in the process; (2) the corrosion rate; and (3) the nature of the corrosion products and their properties (chemical, structural, and protective). For this, numerous study methods can be used, which can be divided into three main classes: analytical methods, electrochemical methods, and optical methods. But in special cases, other methods are used (acoustic, nuclear, etc.).

Electrochemical impedance spectroscopy (SIE) data, were processed with the ZSimpWin software [8], in which the spectra are interpreted by the fit procedure developed by Boukamp - by the smallest squares method. In order to process with this software the data acquired by the VoltaMaster 4 program, this were converted by using the EIS file converter program.

The polarization resistance method was used to evaluate the corrosion rate. This method serves to determine the corrosion current, at the corrosion potential of the metal or alloy, from the linear polarization curve obtained for relatively small overvoltages. The corrosion current determined by this method therefore represents the current that appears at the metal/corrosive medium interface when the metal is immersed in the solution and represents the instantaneous corrosion current.

All measurements were made on freshly cleaned surfaces. Each sample was polished on SiC abrasive paper until granulation 2000, degreased with acetone, washed with distilled water, and kept in bidistilled water until introduced into the electrochemical cell.

Figure 11 shows the linear polarization curves in semi-logarithmic coordinates for the samples studied in the Ringer solution, and in **Table 5**, the parameters of instantaneous corrosion in the same physiological environment are presented.

The corrosion potential, E_{cor} , measured in relation to the potential of the saturated calomel electrode, is the potential at which the oxidation-reduction reactions on the surface of the alloy are at equilibrium; the speed of the oxidation reaction is equal to the rate of the reduction reaction, and the total current intensity is zero. As the potential increases toward more positive values, the speed of the oxidation reaction increases, while the movement of the potential toward negative values, the oxidation process is reduced and the metal is passivized. As a qualitative aspect, the TiMoSi alloy series has a higher corrosion tendency than the TiMoZrTa alloys. The differences are significant, and the presence of zirconia and tantalum seems to cause a decrease in the corrosion rate.

The polarization resistors have high values, which are reflected in very low corrosion rates. The product of "corrosion" in the case of these alloys is mainly titanium oxide, TiO_2 , which is insoluble and adherent to the surface of the alloy. The oxide layer on the surface protects the alloy from the ages of the electrolytic media. In view of this, it can be admitted that in the artificial physiological environment, Ti-based alloys do not corrode but in fact undergo a passivation process. Under these conditions, the parameter V_{cor} —called corrosion rate—is actually passivation speed.

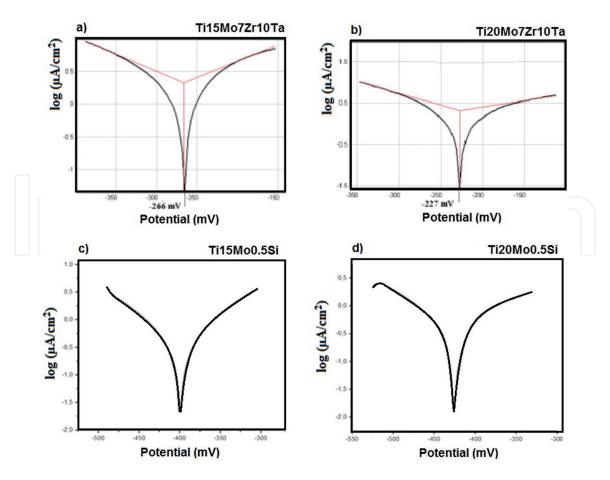


Figure 11.

Linear polarization curves in semi-logarithmic coordinates for titanium alloys developed in Ringer's solution:
(a) Ti15M00.5Si, (b) Ti20M00.5Si, (c) Ti15M07Zr10Ta, and (d) Ti20M07Zr10Ta.

Alloy element	$E_{cor}\left[mV\right]$	$R_p [k\Omega/cm^2]$	$J_{cor} [\mu A/cm^2]$	$V_{cor}[\mu m/an]$	βa [mV]	βc [mV]
Ti15Mo0.5Si	-266	14.91	2.131	20.59	200	-192
Ti20Mo0.5Si	-227	17.71	2.089	20.19	310	-142
Ti15Mo7Zr10Ta	-400.10	46.22	0.37	4.31	92.10	-91.20
Ti20Mo7Zr10Ta	-425.50	50.33	0.38	4.47	130.20	-10.430

Table 5.Instantaneous corrosion parameters for titanium alloys developed in Ringer's solution.

2.6 Surface characterization

One of the requirements of biomaterials is cellular adhesion on the surface of the material, depending on surface energy. The contact angle between a drop of liquid and a solid surface is a sensitive indicator of changes in surface energy and of the chemical and supramolecular structure on the surface. Specialty studies in domain indicated that contact angle measurement is important for the study of cell adhesion to the surface, being the one that characterizes the hydrophobicity of the studied material [21, 22].

Measurement of the contact angle (**Figure 12**) is an experimental technique used to evaluate the hydrophilic or hydrophobic character of the surfaces. Surfaces can be classified as hydrophilic or hydrophobic reported at 90°. If the angle of contact is between 0 and 90°, the material is hydrophilic, and if the angle of contact is between 90 and 180°, material is hydrophobic.

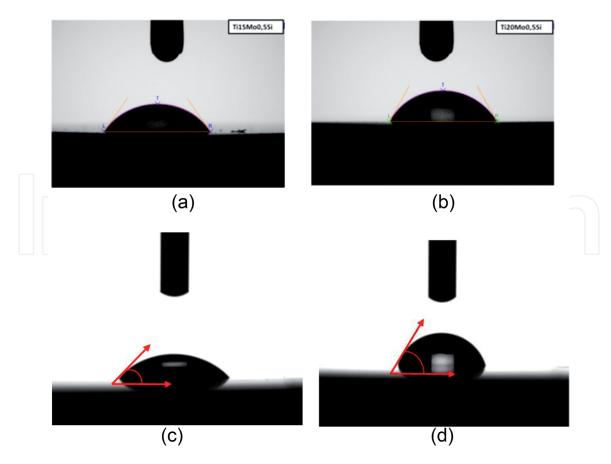


Figure 12.Images of water droplet on the surface of the elaborated alloys: (a) Ti15M00.5Si, (b) Ti20M00.5Si, (c) Ti15M07Zr10Ta, and (d) Ti20M07Zr10Ta.

Alloy	Ti15Mo0.5Si	Ti20Mo0.5Si	Ti15Mo7Zr10Ta	Ti20Mo7Zr10Ta
Liquid used	water	water	water	water
Contact angle (°)	64.40	50.00	45.64	70.72

 Table 6.

 Water contact angle values on the surface of elaborated titanium alloys.

The equipment used allows the determination of the surface tension of the liquids and of the free surface energy of the solid. The principle of measuring the angle of contact consists in placing a drop of water with a microsurgery syringe with the drop volume of $4 \,\mu$ l. Drop lighting is made from behind and recorded from the opposite side with a digital camera. The image obtained is further analyzed through the FAMAS program, a KYOWA integrated goniometer software.

Ten measurements of the contact angle (θ) for each experimental alloy were performed, and the value presented is the average of the measurements made, with a maximum error of $\pm 1^{\circ}$. The average value of the contact angle for each alloy is shown in **Table 6**.

All investigated alloys have a contact angle of less than 90°, thus having a hydrophilic character, which means a high adhesion of the cells to the surface of the alloys.

From the data obtained for the analyzed titanium alloy surfaces, it follows that the value of the highest arithmetic mean of the alloys is recorded at the level of contact angle with water on the surface of the Ti15Mo7Zr10Ta alloy, and the smallest level was Ti20Mo7Zr10Ta alloy, this alloy having a more pronounced hydrophilic character.

3. Conclusions

Metals have traditionally been used to make implants subjected to high loads in the human body, used in various applications. They are known for their high resistance to wear, ductility, hardness, corrosion, and biocompatibility.

For a biomaterial to be functional for an extended period of time in the body, it should be nontoxic and engage in an adequate response with the body, so that it can fulfill its purpose.

The preliminary investigations presented in this chapter for the elaborated titanium alloys revealed the beneficial influence of some stabilizing β elements (Mo, Ta, and Si).

The alloys developed by the proposed method have the advantage of a modulus of elasticity close to that of the human bone and a good corrosion resistance in the simulated biological fluids. According to the obtained values for corrosion and the mechanical properties, the newly developed alloys, for a Young modulus, the value is the closest to the bone (from 19 to 77 GPa our alloys, C.p. Ti is 105 GPa, and the rest are higher, where the bone is 17 GPa) from all the commercial known alloys, and TMZT systems have the lowest corrosion rate. Also, according to the contact angle, the surfaces of the obtained alloys are susceptible for cell development.

Because improving the properties of biomaterials is a necessity to reduce the failure rate of implants in human tissue, we can say that the alloys developed in this chapter can be successful candidates for orthopedic implants, thanks to the stabilizing β elements.



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