POLITEHNICA UNIVERSITY OF BUCHAREST

DOCTORAL SCHOOL OF
MATERIALS SCIENCE AND ENGINEERING

DOCTORAL THESIS

Design, development and characterization of new biocompatible β-Ti alloys

SUMMARY

Doctoral student: Stefan Ioan GHICA

Doctoral advisor: Prof. dr. ing. Mihai BUZATU

BUCHAREST

2023

POLITEHNICA UNIVERSITY OF BUCHAREST

DOCTORAL SCHOOL OF

MATERIALS SCIENCE AND ENGINEERING

Design, development and characterization of new biocompatible β-Ti alloys

SUMMARY OF DOCTORAL THESIS

Doctoral student: Stefan Ioan GHICA

Doctoral advisor: Prof. dr. ing. Mihai BUZATU

BUCHAREST

2023

ABSTRACT

Obținerea de aliaje metalice biocompatibile reprezintă o provocare tehnologică deoarece este greu să realizezi o piesă metalică care să posede proprietăți mecanice adecvate și să fie acceptată de către țesutul din vecinătate fară a-l irita. Teza de doctorat este structurată în trei părți: prima parte cuprinde o analiza a literaturii de specialitate privind materialele metalice biocompatibile; partea a doua este dedicata studiilor și cercetărilor experimentale privind noi aliaje biocompatbile din sistemul Ti-Mo-W; partea a treia contine concluzii finale, contribuții originale și direcții de continuare a cercetării. Capitolele 4 și 5 consacrate studiilor și cercetărilor experimentale cuprind proiectare, elaborarea și testarea a două aliaje din familia β-Titan (Ti15MoxW și Ti19MoxW). Metoda de proiectare a aliajelor utilizată are la bază calcule orbital moleculare ale structurii electronice. Procesul de elaborare a aliajului Ti-xMo-yW a fost realizat în echipamente de retopire cu arc în vid (VAR) într-un creuzet de cupru răcit cu apă folosind metale comerciale de înaltă puritate.Probele obținute au fost supuse analizelor de metalografie, microscopie electronică (SEI, EDAX), difracție de raze X, analizelor de coroziune efectuate în mediu de salivă artificială (SA) și în soluție biologică simulată (SBF).

Cuvinte cheie: aliaje biocompatibile, aliaje β-titan, proiectare aliaje, analize metalografice, microscopie electronica, difractie de raze X, analize de coroziune, salivă artificială, soluție biologică simulată

Obtaining biocompatible metal alloys is a technological challenge because it is difficult to make a metal part that possesses adequate mechanical properties and is accepted by the surrounding tissue without irritating it. The doctoral thesis is structured in three parts: the first part includes an analysis of the specialized literature on biocompatible metallic materials; the second part is dedicated to studies and experimental research on new biocompatible alloys from the Ti-Mo-W system; the third part contains final conclusions, original contributions and directions for further research. Chapters 4 and 5 dedicated to experimental studies and research include the design, development and testing of two alloys from the β-Titan family (Ti15MoxW and Ti19MoxW). The alloy design method used is based on molecular orbital calculations of the electronic structure. The process of making the Ti-xMo-yW alloy was carried out in vacuum arc remelting equipment (VAR) in a water-cooled copper crucible using high purity commercial metals. The obtained samples were subjected to metallography, electron microscopy (SEI, EDAX), X-ray diffraction, corrosion analyzes performed in artificial saliva medium (SA) and in simulated biological solution (SBF).

Keywords: biocompatible alloys, β-titanium alloys, alloy design, metallographic analyses, electron microscopy, X-ray diffraction, corrosion analyses, artificial saliva, simulated biological solution

CUPRINS

INTRODUCTION

1. Choosing the research theme: "Design, development and characterization of new biocompatible β-Ti alloys"

Obtaining biocompatible metal alloys is a technological challenge, because it is not easy to make a metal part that is accepted by the surrounding tissue without irritating it, that does not cause excessive inflammatory response and no immunological reaction, or what can be worse, cancer. In addition, the metal alloy must possess adequate mechanical properties (high resistance to breaking, fatigue resistance, modulus of elasticity of values as close as possible to human bone) and high resistance to corrosion in the environment in which it will act.

In 1920, stainless steel appeared (all stainless steels require a minimum of 10.5% chromium) type 316 (18% chromium, 12% nickel, 2% molybdenum, 0.03% carbon) used as a biocompatible material in surgery to fix fractures by plates, rods, screws, femoral support. The major disadvantage of this type of material is the fact that upon prolonged contact with the fluids of the human body - a very corrosive environment (saline conditions and a high temperature), the phenomenon of surface corrosion occurs. Corrosion on the surface of this material leads to the release of heavy metals – Fe, Ni, Cr ions that can cause allergies or other complications.

The second family of biocompatible alloys were the cobalt-chromium alloys that appeared in the early 1930s. These alloys are non-magnetic, resistant to wear and corrosion, and stable at high temperatures. These alloys are still used to make knee, hip, and shoulder prostheses, and in dentistry it is intensively used as a metal frame for partial dental prostheses. Cobalt-based alloys are superior to stainless steels in terms of corrosion resistance, but the corrosion products of Co-Cr-Mo alloys are more toxic than those of stainless steel. The corrosion resistance of these alloys is based on the formation of a thin passivation layer of Cr2O3; however, the corrosion resistance of Co-Cr-Mo alloys does not compare to the corrosion resistance of titanium and its alloys.

The third family of biocompatible alloys is titanium and its alloys. These materials are highly reactive and when exposed to aqueous media or air, they naturally develop a layer of titanium dioxide (TiO2). The TiO2 layer is highly protective and does not allow any further oxidation when implanted in the human body, being highly resistant to corrosive attack. Currently, titanium alloys cover over 70% of the device materials used for biomedical applications; these materials show superior biocompatibility, good corrosion resistance and high mechanical strength, low Young's modulus of elasticity and are well tolerated in the human body. The most studied and at the same time the most used titanium alloy is the Ti6Al4V alloy (with the structure α+β) which in the thesis will be considered a benchmark for comparison. The Ti6Al4V alloy, being often used in medical applications (such as orthopedic implants), but poses a health risk due to the release of toxic Al and V ions that can cause cytotoxicity.

The Ti-15%Mo alloy appeared in the 1950s. Considered a corrosion-resistant titanium alloy, it was proposed to replace nickel-based superalloys. The Ti-Mo alloy belongs to the class of β-titanium alloys. These alloys have a low modulus of elasticity, high corrosion resistance and are well tolerated in the human body. The stability of the β-titanium structure can be improved by adding stabilizing elements; the most important stabilizing element in β-Ti is Mo, followed by V, W, Nb, Hf, Ta, Fe, Cr, Mn, etc.

By choosing the research theme "**The design, development and characterization of new biocompatible β-Ti alloys** ", the aim was to obtain scientific information on new biocompatible materials.

The major objective of the thesis consists in the design, development and characterization of two titanium alloys from the Ti-Mo alloy family:
alloys with the composition Ti15MoxW, i.e. alloys of Ti + 15%Mo + W (5-11% gr. W);
alloys with the composition Ti19MoxW, i.e. alloys of Ti + 15%Mo + W (7-10%W);

The theoretical design of alloys began in the 1990s when Morinaga and his collaborators proposed a method of theoretical design of alloys based on molecular orbital calculations of the electronic structure [1,2]. According to this theory, alloy design allows the prediction of mechanical and corrosion properties in the case of β-Ti alloys, with the help of several parameters: Bo - electronic parameter considering the characterization of the strength of the covalent bond between Ti and the alloying elements (bond order); Md – the energy level of the d orbital, electronic parameter that characterizes the d orbital energy, with reference to the radius and electronegativity of the elements; valence electron ratio e/a; the Molybdenum equivalent of the elements added to the titanium alloy, Moeq.

After the design of the alloys followed their elaboration, structural characterization by specific methods (optical and electronic microscopy, X-ray diffraction) and verification of corrosion behavior in artificial saliva (SA) and in simulated biological solution (SBF).

The doctoral thesis with the title "**The design, development and characterization of new biocompatible β-Ti alloys**" addresses a topical issue - the design, obtaining and testing of new biocompatible materials; these concerns are widespread among materials science researchers.

The research method for the doctoral thesis includes elaboration techniques and physico-chemical investigation methods specific to the analysis of the structure and properties of metallic materials (optical and electronic microscopy analyses, X-ray diffraction, corrosion resistance testing).

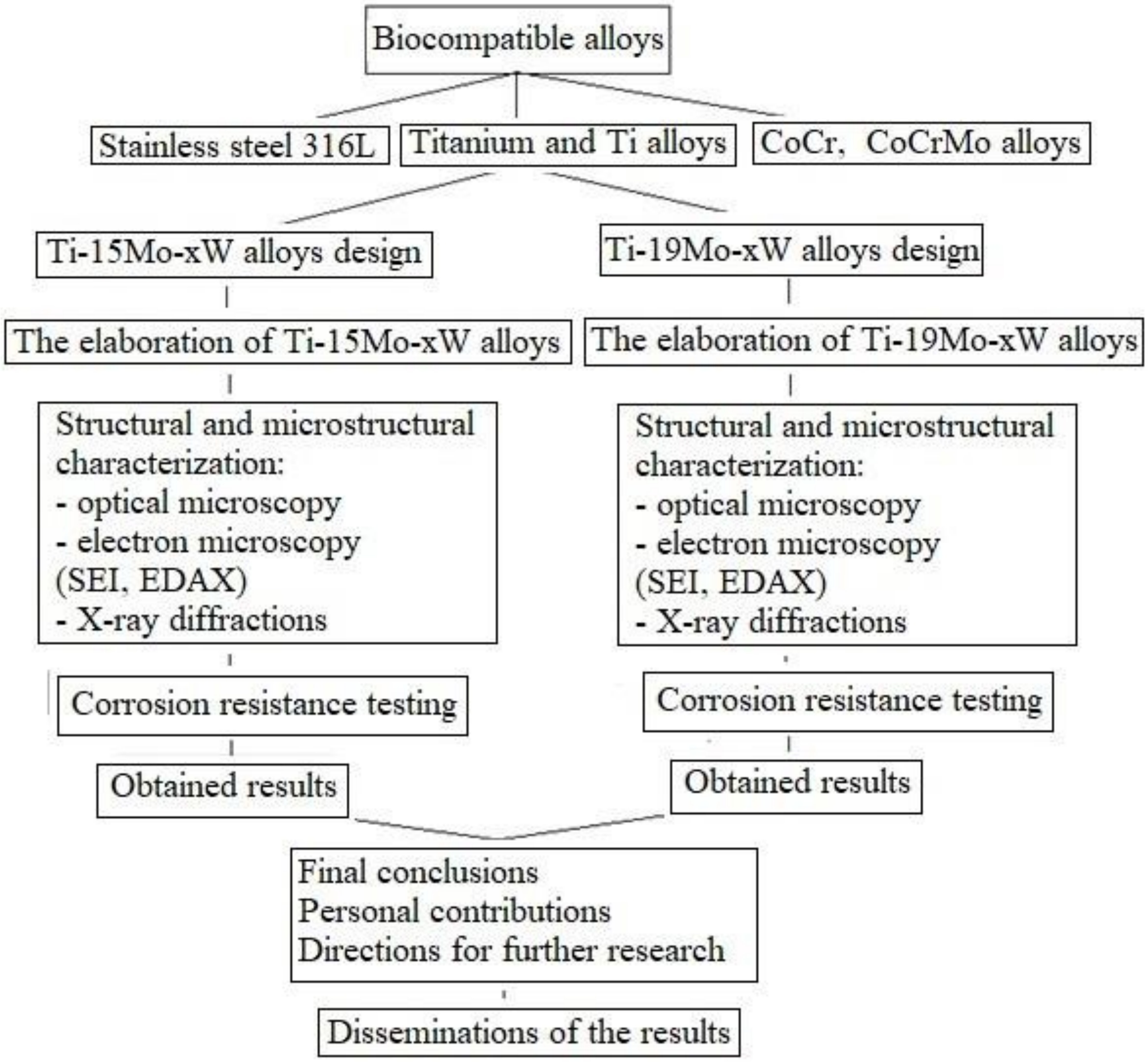

Figure 1. Outline of the research project

PART I. ANALYSIS OF SPECIALTY LITERATURE REGARDING BIOCOMPATIBLE METALLIC MATERIALS

Chapter 1. Biocompatible materials – overview

Today, three types of materials are used for implants and other medical devices: stainless steel, Co-Cr and titanium alloys, and titanium alloys. In dentistry, in addition to the mentioned materials, metals and precious metal alloys (Au, Ag, Pt) are also used.

PART II STUDIES AND RESEARCH ON ALLOYS BIOCOMPATIBLE FROM THE Ti-xMo-yW SYSTEM

Chapter 2. Design of biocompatible alloys from the Ti-xMo-yW system

Phase stability, some mechanical properties and corrosion resistance, in nickel-base alloys (initially in 1964), later titanium, can be predicted by some relations discovered between electron density and atomic (or ionic) radii through a series of calculations.

β-Ti alloys, with the cvc structure, are considered the most suitable biocompatible alloys having a low modulus of elasticity (40...70 GPa, close to the value of bone 20 GPa) and high mechanical strength and corrosion resistance values.

However, titanium alloys are metastable and prone to precipitation of secondary phases, (α, ω), which can increase the elastic modulus values up to approximately 110 GPa [12-16]. In conclusion, due to the metastable nature, these alloys require β-stabilizers, such as Mo, Nb, Ta, etc., so that β-Ti alloys with high mechanical performance and corrosion resistance are generally made in multicomponent alloy systems, which contain both β-stabilizers, such as Mo, Nb, Ta, and elements that lower the elastic modulus values, such as Sn, Zr, and Al [12–16].

According to the alloy design theory, theory developed by M. Morinaga in the 90s, the prediction of mechanical and corrosion properties in the case of β-Ti alloys can be achieved with the help of several parameters:

Bo - electronic parameter considering the characterization of the strength of the covalent bond between Ti and the alloying elements (bond order);

- $B_{O_t} = \sum x_i \cdot B_{O_i}$
- $x_i = \%\, at. of\ i\ element$
- $B_{O_i} = Bond\ order\ for\ element\ i$

Md – the energy level of the d orbital, electronic parameter that characterizes the d orbital energy, with reference to the radius and electronegativity of the elements;

- $M_{d_t} = \sum x_i \cdot M_{d_i}$
- $x_i = \%\, at. of\ i\ element$
- M_{d_i} =*The energy level of layer d for element i*

By design, the characteristics of the alloy can be predicted using these first two electronic parameters: Bo (characterizing the strength of the covalent bond between Ti and the alloying elements) and Md (characterizing the orbital energy d, related to the radius and electronegativity of the elements) [16-17].

These two parameters are theoretically determined in β-Ti with the cvc structure, using the molecular orbital method. $\overline{Bo}$ is a measure of the strength of the covalent bond between Ti and an alloying element, M. $\overline{(Md)}$ is the metal-orbital energy level of the alloying transition metal, M, which correlates well with the electronegativity and metallic radius of the elements.

These values are listed in Table 1, as the calculations have recently been extended to a variety of alloying elements.

For each alloy, the values of $\overline{Bo}$ and ($\overline{Md}$) can be calculated and thus the position and evolution on the ($\overline{Bo} - \overline{Md}$) diagram will provide important information about phase stability, Young's modulus and corrosion behavior.
The stability of the β phase increases with increasing content of β-stabilizing elements, for various binary Ti-M alloys (M = V, Cr, Mo, W, etc.). The more stable the β phase, the lower the Young's modulus; the appearance of the ω phase in the alloy increases the Young's modulus, so its precipitation should be avoided to maintain a Young's modulus as low as possible [3].

After laborious studies and calculations, Morinaga et al. they came to the conclusion that the value of $\overline{Bo}$ should be less than 2.84, which sends us to the lower left part of the diagram ($\overline{Bo} - \overline{Md}$)(fig. 2.2.1.). From this diagram it can be seen that the range of β-Ti type alloys is extended far beyond the (Bo)¯ value of 2.84.

β-type alloys are recognized to be deformable by either slip or shear mechanism, all depending heavily on the stability of the β phase.

In the ($\overline{Bo} - \overline{Md}$) diagram (fig. 2.2.1.), the single β phase region is clearly separated from the β + ω phase region.

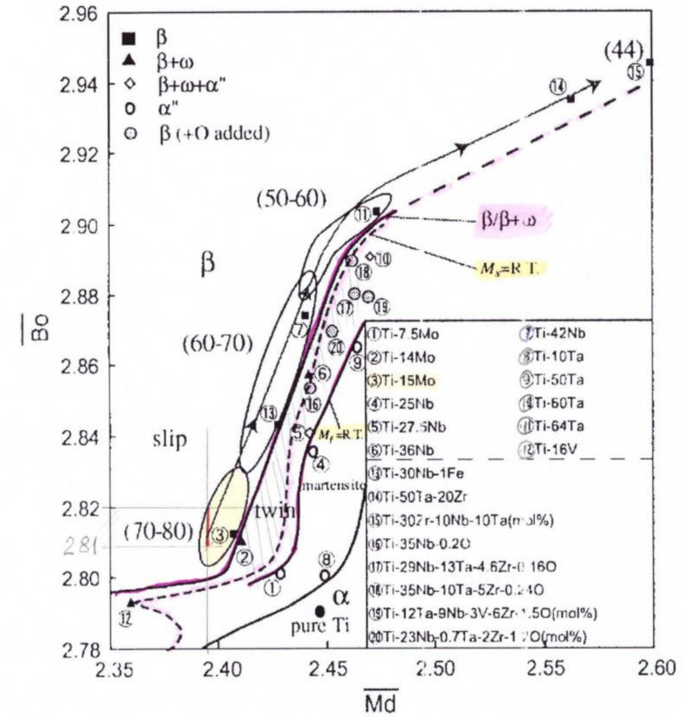

Figure 2.2.1. The extended (Bo)¯-(Md)¯ diagram in which the boundary between the β/β+ω phases is underlined in red together with the beginning and end of transformation (pairs / dislocations), Ms and Mf at room temperature; the value of the Young's modulus (GPa) is given in parentheses for four typical alloys.[13].

At low degrees of deformation (1...5%) macles may appear (disorientations of the crystalline network over short distances); plastic deformation can occur due to dislocations, by sliding (due to network defects).

It is found that the elastic modulus of the alloys decreased with increasing values of Bo and Md in the β titanium alloy region.

At the same time, Morishita et [14] investigating the effects of alloying elements on the corrosion resistance of different types of β-Ti type alloys, both in 10% HCl and 10% H2SO4, came to the conclusion that the alloys containing elements with the order of the covalent adhesion bond between Ti and the alloying elements - Bo - will present a lower active corrosion speed.

These statements are supported by the conclusions of the studies initiated by X.H. Min et al [15] who concluded that crevice corrosion resistance increases linearly with Bo from 2.7900 to 2.8233 in Ti-Mo base alloys.

$$-\frac{\boldsymbol{e}}{\boldsymbol{a}} = \sum_{i=1}^{n} x_i \cdot e_i$$

- $x_i = = \%\, at. of\ i\ element;$
- $e_i = valence\ electrons\ of\ element\ i\ ;$

The formation of the thermal ω phase in titanium alloys has been reported to be predictable by the e/a ratio [18]. The formation of the thermal phase ω reached a maximum at the e/a ratio 4.13 and a minimum at 4.3. When the e/a ratio is greater than 4.3, the β phase becomes the dominant phase. (Qing Wang 2015).

In order to refine the alloy design method known as d-layer electron, C.H. Wang et al. [16] proposed in 2019 a correlation between the valence electron ratio ($\overline{e/a}$) and the difference $\overline{\Delta \mathrm{r}} = \sum_i^n c_i\,(r_i - r_{Ti})$ (the sum of the multiplication of the atomic fraction of element i, with the difference between the atomic radii of alloying element i and that of the titanium atom).

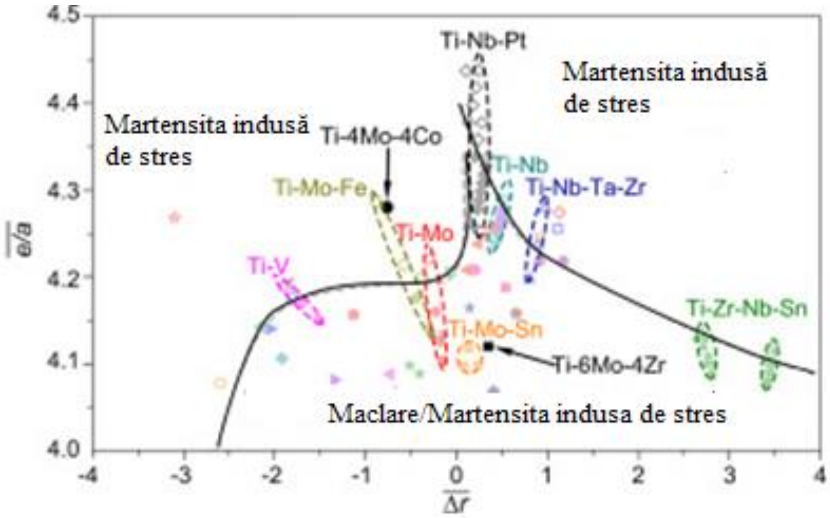

Fig. 2.2.2. Diagram (e/a)¯- (Δr)¯for the delimitation of deformation mechanisms [16].

With the help of this correlation, it was possible to draw diagrams (e/a)¯- (Δr)¯in which the domain of dislocation slip deformation (stress-induced martensite) can be accurately delimited from the domain of deformation by maceration.

From the diagram it can be seen that the domain of slip deformation, due to dislocations (Slip) is more extensive than the mixed domain Twinning deformation (Twinning)/ Martensite induced by SIM stress), positioning itself at values (e/a)¯< 4.2 and when (Δr)¯> -2.5.

It is also noted that the range of deformation through twinning (Twinning)/SIM stress-induced martensite) presents a maximum when (Δr)¯is close to the zero value, after which the range narrows as (e/a)¯increases above 4.2.

The diagram is suggestive because it shows clear differences in plastic deformation properties for two β-Ti alloys located in the same domain of the (Bo)¯-(Md)¯diagram.

In the diagram it can be seen that alloys such as Ti-(10...15% gr.) Mo, or Ti-9Mo-6W are found in the mixed field of deformation by twinning (Twinning)/ Martensite induced by SIM stress), while with the increase in molybdenum content Ti-20%gr. Mo, the alloy stabilizes in the range of deformation by sliding, due to dislocations.

4) **Mo equivalent;**

The Moeq method evaluates the stability of β-Ti (quantitatively) using the Molybdenum equivalent of the elements added to the titanium alloy (stabilizers and elements to lower the elastic modulus values).

Bania [16], established empirically that in binary systems, alloys with Moeq > 10 % gr. Mo a single β phase could be formed. The proposed equation is:

- $(Moeq)_B = 1.0\ Mo + 0.67\ V + 0.44\ W + 0.28\ Nb + 0.22\ Ta + 2.9\ Fe + 1.6\ Cr + 0.77\ Cu + 1.11\ Ni + 1.43\ Co + 1.54\ Mn + 0\ Sn + 0\ Zr - 1.0\ Al$ (wt pct).

The formula attempts to measure the overall stability of the β-Ti phase by comparing the elemental contributions to that of the major stabilizer of the β-Ti phase, which is Mo (summation of binary influences).

Low modulus β-Ti alloy systems are multicomponent with complex interactions. This required a revision of the Mo equivalent formula to take into account atomic interactions in multicomponent systems.

The formula proposed by Zhou [16] for Moeq is:

-$(Moeq)_Z = 1.0\ Mo + 0.74\ V + 0.50\ W + 0.39\ Nb + 0.28\ Ta + 2.2\ Fe + 1.69\ Cr + 0.85\ Cu + 1.22\ Ni + 1.57\ Co + 1.69\ Mn + 0\ Sn + 0\ Zr - 1.0\ Al$ (wt pct).

Now, the β_c value of Mo is set at 11 wt%.

In 2015 Qing Wang proposed a new expression for calculating equivalent (Moeq)Q, which uses the slopes of the boundary lines between the β and (α + β) phase zones in the Ti-M binary phase diagrams. This (Moeq)Q quantifies that the stability of β-Ti is improved, when the β-phase area is increased with a β-Ti stabilizer.

The formula proposed by Qing Wang [16]:

- $(Moeq)_Q = 1.0\ Mo + 0.74\ V + 1.01\ W + 0.23\ Nb + 0.30\ Ta + 1.23\ Fe + 1.10\ Cr + 1.09\ Cu + 1.67\ Ni + 1.81\ Co + 1.42\ Mn + 0.38\ Sn + 0.34\ Zn + 0.99\ Si - 0.57\ Al$ (% at.), or
- $(Moeq)_Q = 1.0\ Mo + 1.25\ V + 0.59\ W + 0.28\ Nb + 0.22\ Ta + 1.23\ Fe + 1.84\ Cr + 1.50\ Cu + 2.46\ Ni + 2.67\ Co + 2.26\ Mn + 0.30\ Sn + 0.47\ Zr + 3.01\ Si - 1.47\ Al$ (% gr.),

where the equivalent coefficient of each element is the ratio of the slope of the boundary line [β/(α + β)] of the Ti-M binary phase diagram to that of Ti-Mo. [16].

This $(Moeq)_Q$ fairly accurately assesses the critical stability limit of multicomponent β-Ti alloys with low Young's moduli. The lower critical limit for stabilization of the β phase has the value $(Moeq)_Q = 6.25$ at. Pct or 11.8% by weight Mo.

The values of the molybdenum equivalent – Moeq and those of the bond order – Bo, are closely related to the concentration of a new alloying element added (stabilizing the β phase) in a Ti-Mo alloy

In general, the value of the modulus of elasticity for β-Ti alloys increases with increasing molybdenum equivalent (Moeq). It therefore follows that the smallest modulus of elasticity E should be reached by alloys with $(Moeq)_Q$ values close to the critical limit of β-phase formation in multicomponent alloys. Problems arise in the case of precipitation of the ω phase (especially in Ti-Mo alloys); by careful design, the ω phase can be avoided, moving the parameters into the stability zone of the β phase.

From the Ti-Mo binary equilibrium diagram it is observed that the monotectoid point is at 12% at. (21.46 % gr.).

Chapter 3. Research methodology and equipment used for research biocompatible alloys from the Ti-xMo-yW system

To carry out the experimental research works at the laboratory level, a varied range of apparatus and devices were used. The structural and microstructural analysis of the materials was carried out in the laboratories of the Polytechnic University of Bucharest

Chapter 4. Studies and experimental research on Ti-15Mo-xW alloys

The first family of titanium alloys that we focused on was selected from the Ti-15%Mo family, to which we added increasing proportions of tungsten (5-11% wt. W). From the very beginning, analyzing the specialized literature (documentation started with specialized articles published in 2015-2017) the intention was to obtain an alloy with high mechanical characteristics – the smallest possible modulus of elasticity (i.e. close to that of human bone, 20-30 Gpa), and resistant to corrosion. These criteria led us to the conclusion that we need to make a titanium alloy with a β-Ti structure, stable and with a corrosion resistance comparable to the established Ti-6Al-4V alloy. Due to the α + β microstructure, the Ti-6Al-4V alloy has excellent mechanical properties (high strength of 800-900 Mpa and a modulus close to 100 Gpa) [4-6]. The Ti-6Al-4V alloy has some drawbacks related to corrosion. The phenomenon of corrosion consists in the damage of the metal or alloy due to the electrochemical attack of the environment and can lead to the release of unwanted and potentially toxic ions in the biological environment. Unfortunately, the passive oxide films of the additives (Al2O3 and VO2) that form on the surface of the alloy are less stable than TiO2, which can lead to corrosion of the alloy. Vanadium in the form of V_2O_5 is cytotoxic and induces adverse tissue reactions [7]. Aluminum plays a role in neurodegenerative diseases [8, 9, 10 and 11]. However, Ti6Al4V is the most commonly used titanium alloy for implants [12, 13 and 14].

Recently, new titanium alloys with comparable mechanical properties (with more stable beta phase and low elasticity), but in which vanadium was replaced by Ta, Nb, Mo, Zr in alloys such as: Ti25Nb10Zr, Ti6Al7Nb, Ti5Al2,5Fe, Ti5Al3Mo4Zr, which were then investigated [15, 16, 12].

The experimentally obtained Ti-Mo-W alloys presented in this study are novel and can be considered as a possible candidate for use in medical applications. This metal has 6 valence electrons, which can lead to an alloy with a high electron density (e/a) to influence the modulus of elasticity in the direction of its decrease.

In this sense we proposed the preparation of Ti15Mo type compositions (5-11% wt. W) to obtain a stable β-Ti phase (body-centered cubic) with low elastic modulus and good mechanical and corrosion characteristics. As can be seen from Fig. 4.1. the lowest modulus of elasticity for Ti-Mo alloys was identified in the alloys with 8 % at. Mo (ie Ti15%gr.Mo) on which we developed the research.

In the production of β-titanium alloys, there are many β-phase stabilizing elements that can be added to the alloy composition. The degree of stabilization of the β phase depends on the respective elements. Mo is the most important stabilizing element of the β phase. The equivalent of Mo (Moeq) indicates the stability of the β phase [18-22].

From Fig. 4.2. it can be seen that starting with Ti-12 % at. Mo (Ti-19 wt % Mo) the ω-Ti phase was no longer recorded in the diffractogram. We will insist on this aspect in chapter 5. The Ti-15Mo-(5-11) W alloy is a new alloy, little studied at the time the research began.

4.1. Design of Ti-15M-xW alloys

The first parameter analyzed was Bo – electronic parameter that considers the characterization of the strength of the covalent bond between Ti and the alloying elements (bond order).

The values (calculated with the formulas below, in atomic percentages), for this parameter were processed in an Excel program and presented graphically in fig. 4.1.1.

Table 4.1.1. Calculated values of $\overline{Bo}$ and $\overline{Md}$ for Ti-15Mo-xW alloy.

	Ti		Mo		W		$\overline{Bo}$	$\overline{Md}$
Aliaj	% gr.	% at.	% gr.	% at.	% gr.	% at.		
Ti-15Mo-11W	74	87,7317769994	15	8,872642042	11	3,3955809586	2,825597509	2,3911455311
Ti-15Mo-9W	76	88,5499605078	15	8,7197198884	9	2,7303196038	2,82295649	2,3943834628
Ti-15Mo-7W	78	89,340418688	15	8,5719797243	7	2,0876015878	2,82039497	2,3975116726
Ti-15Mo-5W	80	90,1045373206	15	8,4291625379	5	1,4663001415	2,817923719	2,4005356445
Ti-15Mo	85	91,9078926246	15	8,0921073754	-	-	2,812091453	2,4076723581

From diagram 4.1.1. it is observed that the value of (Bo)¯increases from 2.812091453 ((Ti-15Mo) to 2.817923719 by adding 5% wt. W (Ti-15M-5W) reaching 2.825597509 for the alloy with 11% gr. W (Ti-15M-11W).

X.H.Min et al. published in 2011 [16] an article in which they presented the results of research undertaken to optimize mechanical properties and corrosion resistance by controlling two design parameters (Bo) and (Moeq) in the case of Ti-Mo system alloys, (Ti -15Mo-5Zr and Ti-15Mo-5Zr).

Their conclusions refer to the Ti-Mo alloy family and claim that corrosion resistance shows a linear increase with increasing (Bo)¯((Bo)¯must have a value greater than 2.8126). In the alloys studied and presented in the thesis, in Ti-15Mo alloys -5...11% gr. W, the value of (Bo)¯satisfies this requirement.

The increase in the value of (Bo)¯from 2.81 to 2.82 is transposed by the fact that the stability of the β-Ti phase increases (fig. 2.2.1.), the position on the diagram moving away from the limits of the appearance of the ω phase . A more stable β-Ti phase means an alloy with a low elastic modulus.

This fact will be confirmed by the x-ray diffraction analysis to which the alloy was subjected (Fig. 4.3.1.).

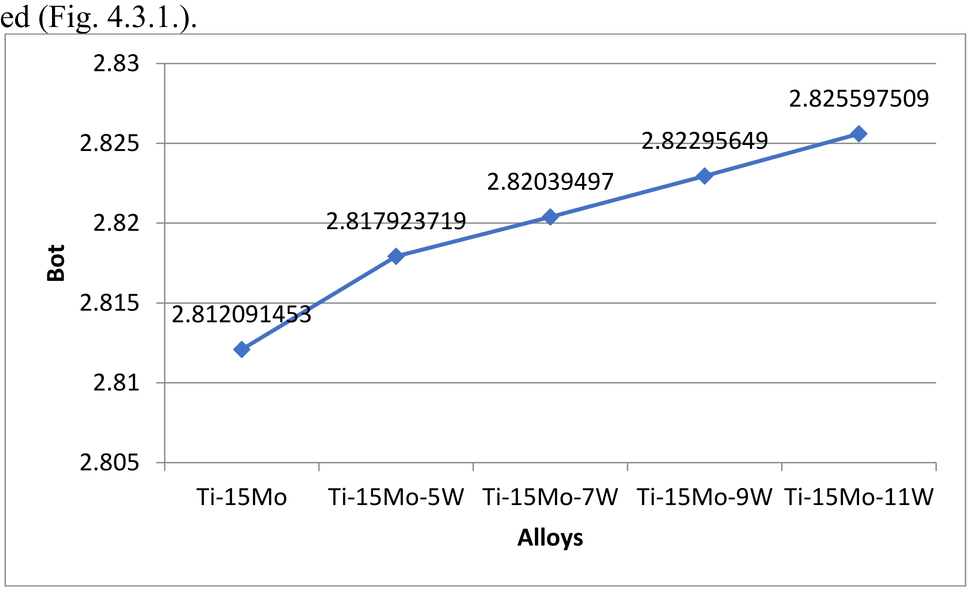

Fig. 4.1.1. The evolution of the parameter $\overline{Bo}$ according to the chemical composition of the Ti-15Mo-xW alloy.

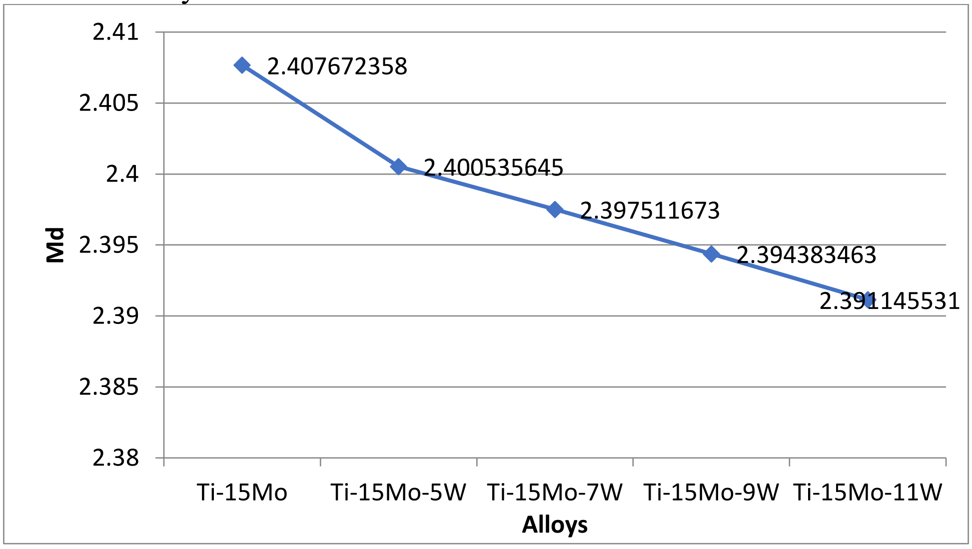

Fig. 4.1.2. The evolution of the $\overline{Md}$ parameter according to the chemical composition of the Ti-15Mo-xW alloy.

The values of Bo and Md calculated allow locating and anticipating the evolution of the behavior of the alloy on the Bo-Md diagram; thus we can learn important information about phase stability, Young's modulus and corrosion behavior.

The stability of the β phase increases with increasing content of β-stabilizing elements, for various binary Ti-M alloys (M = V, Cr, Mo, W, etc.). The more stable the β phase, the lower the Young's modulus; the appearance of the ω phase in the alloy increases the Young's modulus, so its precipitation should be avoided [3].

After some laborious studies and calculations, Morinaga et al. they concluded that the value of $\overline{Bo}$ should be less than 2.84, which sends us to the lower left of the $\overline{(Bo)}$-$\overline{(Md)}$ diagram.

From diagram 2.2.1. it is observed that the range of β-Ti type alloys is extended far beyond the value of $\overline{Bo}$ of 2.84. The studied alloys are positioned in the stable β range, well below the established limit value of $\overline{Bo}$ of 2.84.

At the same time, valuable researchers in the field of alloy design, such as Morishita, X.H. Min concluded that crevice corrosion resistance increases linearly with Bo from 2.7900 to 2.8233 in Ti-Mo base alloys. The design calculations performed showed that the Ti-15Mo-xW alloys fall within these limits. Confirmation of good corrosion behavior came after performing corrosion tests in the two environments: artificial saliva (SA) and simulated biological solution (SBF) presented in paragraph 4.3.

Table 4.1.2. Calculated values of the parameter (e/a) for Ti-15Mo-xW alloys.

	Ti		Mo		W		$\frac{e}{a}$
Aliaj	% gr.	% at.	% gr.	% at.	% gr.	% at.	
Ti-15Mo-11W	74	87,7317769994	15	8,872642042	11	3,3955809586	4,24536446
Ti-15Mo-9W	76	88,5499605078	15	8,7197198884	9	2,7303196038	4,229000789
Ti-15Mo-7W	78	89,340418688	15	8,5719797243	7	2,0876015878	4,213191626
Ti-15Mo-5W	80	90,1045373206	15	8,4291625379	5	1,4663001415	4,197909254
Ti-15Mo	85	91,9078926246	15	8,0921073754	-	-	4,161842147

The calculated values for the ratio (e/a) for Ti-15Mo-xW alloys are presented in table 4.1.2. and the evolution of the ratio of valence electrons according to the chemical composition of the alloy is included in fig. 4.1.3.

The evolution of this parameter, (e/a) is very important, since the formation of the thermal phase ω in titanium alloys has been reported to be predictable by the e/a ratio [18].

In [13] it is mentioned that the stability of the bcc structure in binary alloys of Ti or Zr (having bcc structure) is strongly related to the control of the number of valence electrons, to about 4.20–4.24 to obtain a low Young's modulus material. The alloys studied, from the Ti-15Mo-xW family with W > 7%gr. Fits into this condition.

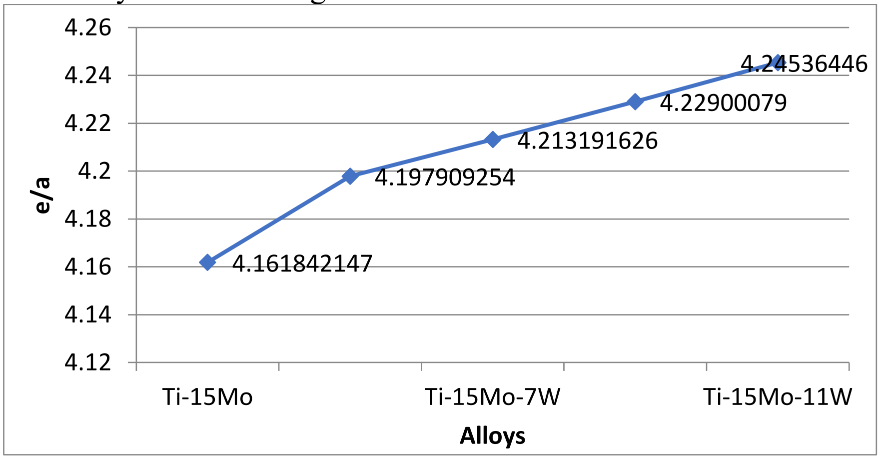

Fig. 4.1.3. Evolution of the parameter (e/a) according to the chemical composition of the Ti-15Mo-xW alloy.

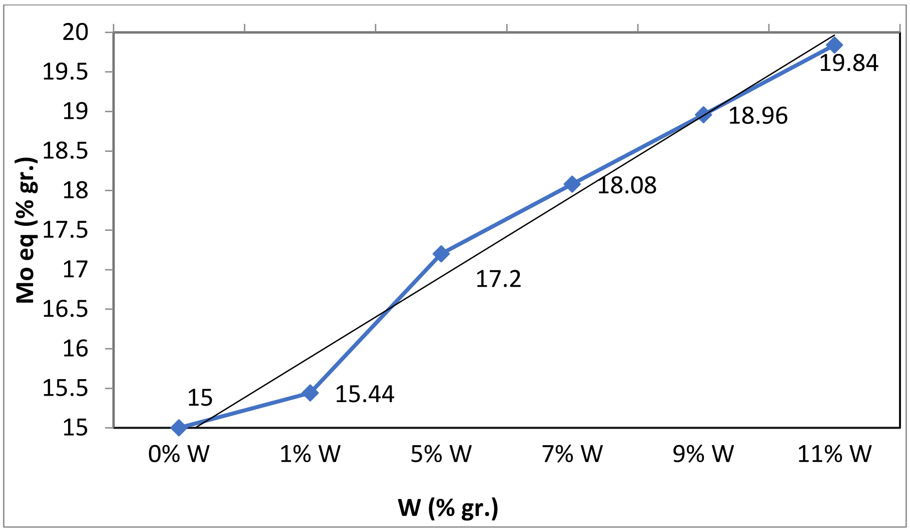

Fig. 4.1.4. The evolution of the parameter (Moeq) according to the chemical composition of the alloy

Ti-15Mo-xW, calculated according to Bania.

Referring to the parameter (Moeq), X.H.Min et al.[40] they came to the conclusion that for a successful combination between strength, ductility and corrosion resistance, the value of the parameter (Moeq) must be designed at values between 15.3 and 18.7% by weight, values very close to those calculated and presented in the thesis.

From the Ti-Mo binary equilibrium diagram it is observed that the monotectoid point is at 12% at. (21.46 % gr.), fig. 2.2.5. – Ti-Mo equilibrium diagram.

4.2. Development of Ti-15Mo-xW alloys

The fabrication process of the Ti-15Mo-xW alloys was carried out in vacuum arc remelting (VAR) equipment in a water-cooled copper crucible (VAR model 900 ABD MRF) using high purity commercial metals.

The temperature reached in this type of furnace is over 3500°C, high enough for the melting of selected alloys (melting and mixing).), which contain metals with a high melting point (Ti –124 1668°C; Mo–2623oC; W–3422°C) [26 – 29].

The chemical composition of the Ti-15Mo-xW alloys obtained after melting in the VAR furnace is presented in table 4.2.2.[19-22]

Table. 4.2.2. The chemical composition of the elaborated Ti-15Mo-xW alloys.

Nr. Crt.	**Tipul de aliaj**	**Compozitia chimica, % gr.**				
		W	Mo	Al	V	Ti
1	Ti15Mo11W	11,08	13,78	-	-	75,14
2	Ti15Mo9W	9,21	15,15	-	-	75,64
3	Ti15Mo7W	7,29	14,97	-	-	77,74
4	Ti15Mo5W	5,75	15,67	-	-	78,59
5	Ti6Al4V	-	-			89,81

4.3. Characterization of Ti-15MoxW alloys

Optical and electron microscopy images show that the alloy is homogeneous and has an average grain size of 1.53 mm.

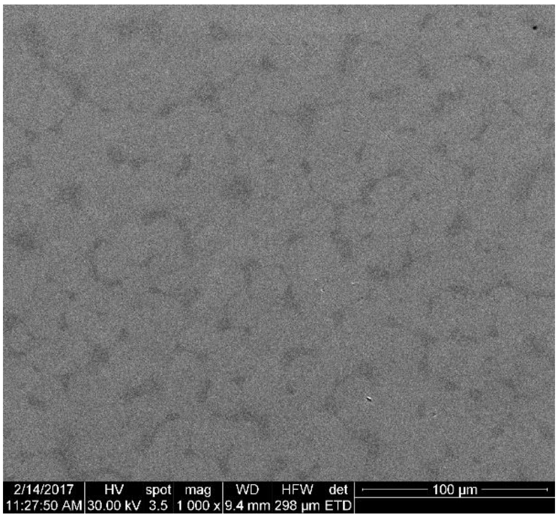

Fig. 4.3.2. SEI image of the microstructure of the Ti15Mo9W alloy (x1000).

The chemical composition of the alloys was confirmed by EDX electron microscopy analyses.

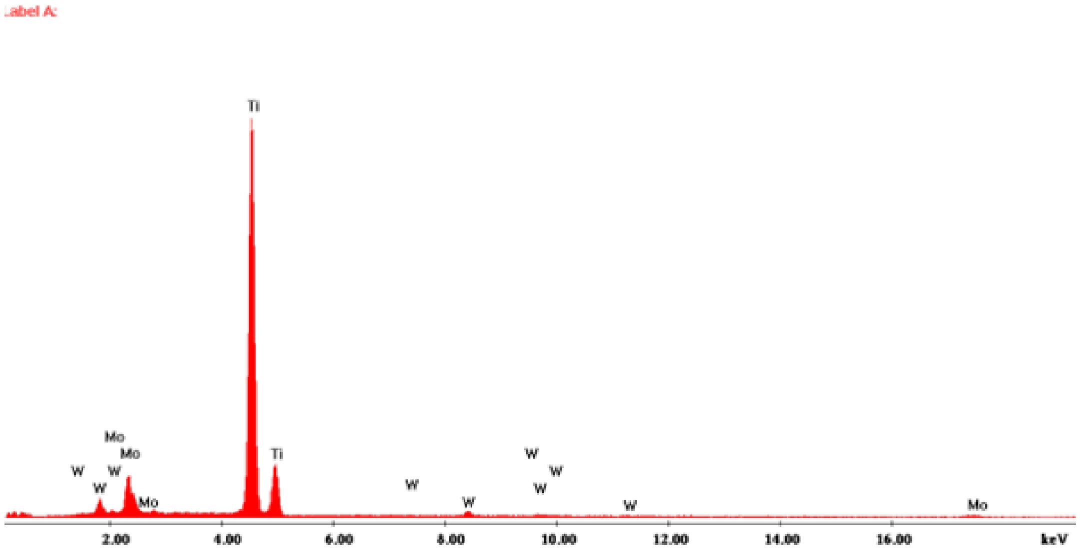

Fig. 4.3.3. EDX analysis; the presence of Ti, Mo, W is well defined.

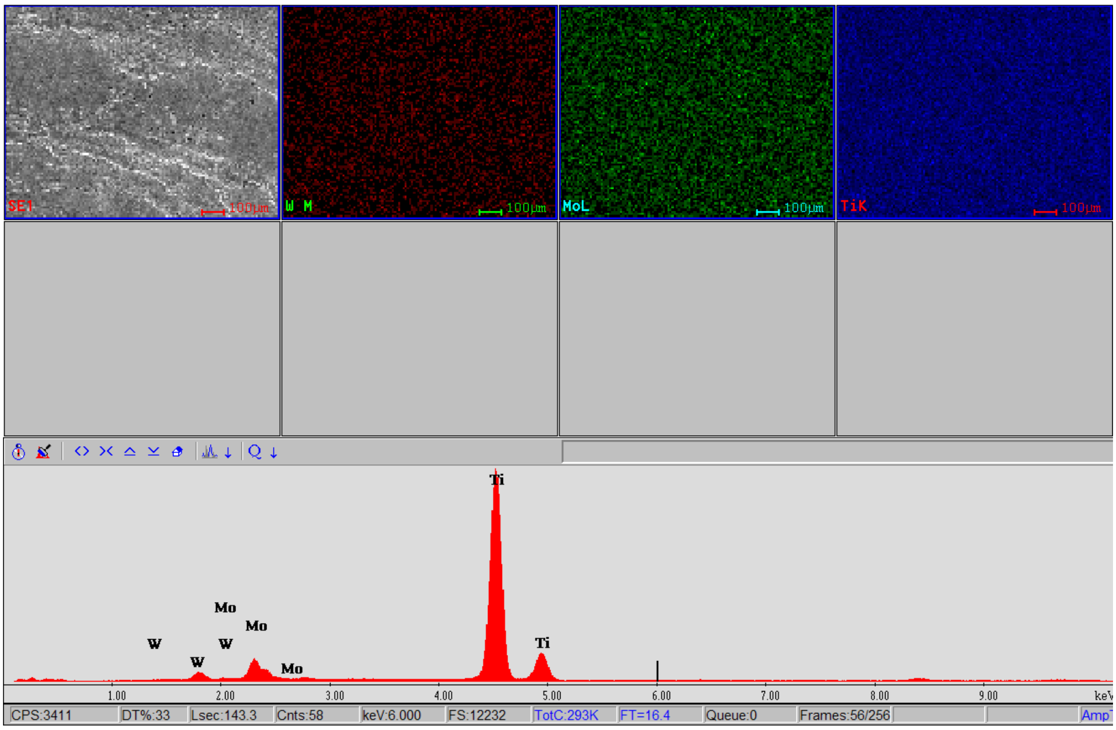

Fig. 4.3.4. Distribution of Ti, Mo, W elements on the analyzed surface.

The obtained structure is of the β-Ti type and was confirmed by X-ray diffraction analyses.

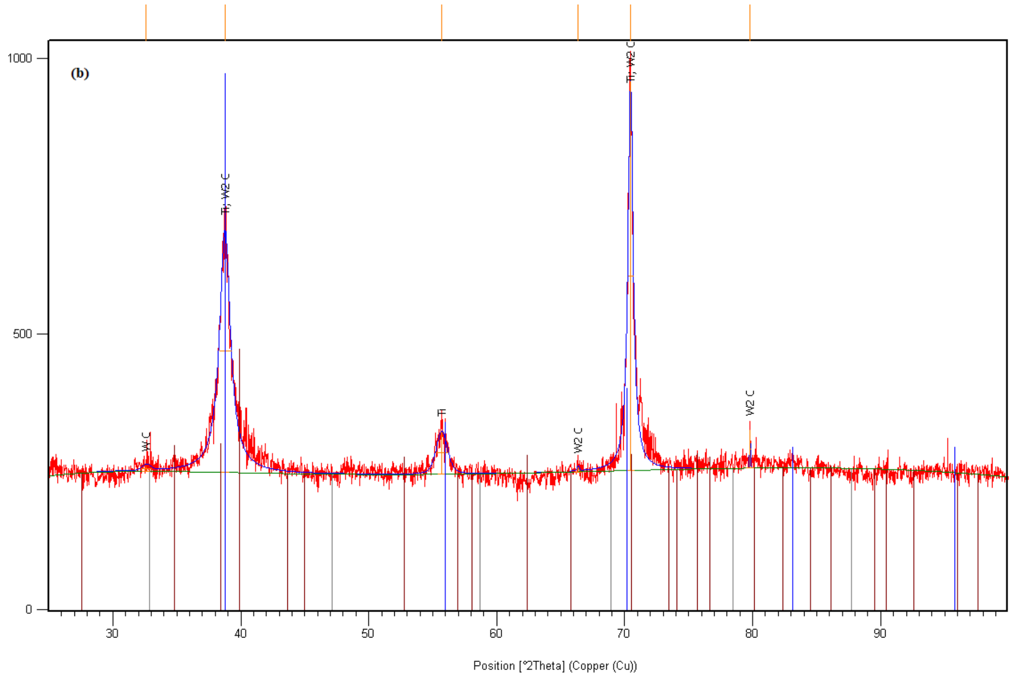

Fig. 4.3.5. The results of the X-ray diffraction investigation of the Ti15Mo9W alloy; (4) interplanar distances; (b) characteristic compounds.

Table 4.3.1. Table of interplanar distances recorded on the diffractogram 4.3.1. (a)

No.	H	k	l	d (A)	2Theta (deg)	I (%)
1				**2,75111**		
WC	1	0	0	2,72300	32,865	100
2				**2,32105**		
β-Ti	1	1	0	2,32140	38,759	100
W_2C	0	0	2	2,34050	38,430	23
3				**1,64854**		
β-Ti	2	0	0	1,64150	55,973	13,1
4				**1,40756**		
W_2C	3	0	0	1,41770	65,823	0,1
5				**1,33531**		
β-Ti	2	1	1	1,34030	70,160	20,8
W_2C	-1	-1	3	1,33470	70,498	13,5
6				**1,20100**		
WC	2	1	0	1,21780	78,475	21,8

Corrosion resistance using Fusayama Meyer artificial saliva (SA) as electrolyte

The corrosion resistance was determined by the linear polarization technique [1,2, 19-22]. This technique consists in drawing linear polarization curves involving the following steps:

- measurement/monitoring of the open circuit potential (EOC), for a duration of 6 hours;
- plotting the curves of the linear polarization curves from -200 mV (vs OCP) to +200 mV (vs OCP) - Tafel curves, with a scan rate of 0.167 mV/s.

The corrosion resistance evaluation tests were carried out using a Potentiostat/ Galvanostat (model PARSTAT 4000, manufactured by Princeton Applied Research, USA) to which a low current module (VersaSTAT LC, manufactured by Princeton Applied Research) was connected (Fig. 4.3.6.), and the potentiodynamic curves (Table) were acquired using the VersaStudio software

To carry out the tests, a corrosion cell was used (Fig. 4.3.7.) which consists of a calomel saturated electrode (SCE) - reference electrode, a platinum electrode - recording electrode and the working electrode which consisted of the experimental samples to be investigated (Fig. 4.3.7.). During the corrosion tests, the electrochemical cell was placed in a Faraday cage in order to eliminate interferences due to electromagnetic fields[18-22].

The tests were performed at the temperature of the human body (37±0.5°C) using a CW-05G heating and recirculation bath produced by Jeio Tech.

The tests were performed using Fusayama Meyer artificial saliva (SA) as electrolyte (composition: 0.4 gl-1NaCl, 0.9 gl-1 KCl, 1 gl-1 urea, 0.69 gl-1 NaH2PO4, 0.795 gl-1 CaCl*2H2O) at pH=5.2. [18]

The tested samples were coded within the corrosion resistance tests and this coding can be found in Table 4.3.3 [1,2, 19-22]. Table 4.3.4.

The main electrochemical parameters of the corrosion process of Ti15MoxW samples in (SA)[1,2,19-22]

Nr. crt.	**Proba**	**E_{cor} (mV)**	**i_{cor} (nA/cm^2)**	**β_c (mV)**	**β_a (mV)**	**R_p (kΩxcm^2)**	**CR (µm/an)**
1.	Ti15Mo11W tip 1	-204,6	24,155	100,6	218,2	1239,55	0,247
2.	Ti15Mo9W tip 2	107,7	66,577	234,6	335,8	902,17	0,688
3.	Ti15Mo7W tip 3	-269,5	15,364	52,2	135,4	1067,65	0,150

4.	Ti15Mo5W tip 4	-163,4	39,923	78,4	357,5	700,47	0,409
5.	Ti6Al4V	33,92	42,693	130,94	163,88	932,78	0,390

Evaluation of the corrosion resistance of some Ti15MoxW alloys in simulated biological solution (SBF)

The tests were performed using simulated biological solution (SBF) (composition: 7.996 g/L NaCl, 0.350 g/L NaHCO3, 0.224 g/L KCl, 0.228 g/L K2HPO4·3H2O, 0.305 g/L MgCl2·6H2O, 40 mL 1 M-HCl, 0.278 g/L CaCl2, 0. .071 g/L Na2SO4, 6.057 g/L (CH2OH)3CNH2)) at pH=7.4 [21,22].

Table 4.3.6. The main electrochemical parameters of the corrosion process of Ti15MoxW samples in (SBF) [21,22].

Nr. crt.	**Proba**	**E_{cor} (mV)**	**i_{cor} (nA/cm^2)**	**β_c (mV)**	**β_a (mV)**	**R_p (kΩxcm^2)**	**CR (μm/an)**
1.	Ti15Mo11W tip 1	-293,2	52,919	155,72	141,74	609,645	0,542
2.	Ti15Mo9W tip 2	51,8	105,649	258,10	273,12	546,109	1,093
3.	Ti15Mo7W tip 3	-282,6	54,955	148,51	85,37	428,885	0,537
4.	Ti15Mo5W tip 4	-333,1	28,862	28,55	541,99	408,642	0,296
5.	Ti6Al4V	-186,2	35,415	120,98	199,62	924,836	0,321

Chapter 5. Studies and experimental research on Ti-19Mo-xW alloys

Since the stable β -Ti phase was identified at a concentration above 8% at. Mo (15% wt. Mo), we increased the Mo content to 11% at. (19% gr. Mo), keeping the W content at the same values (2-3% at.W, equivalent to 7-19%gr.W). The addition of a sufficient amount of molybdenum gives titanium a very good corrosion resistance [50, 54]. In several studies [56] it has been observed that a minimum percentage of 15% by weight of Mo can lead to an increase in corrosion resistance in biological environments at high temperatures for titanium alloys [57-66].

It has been observed that the phase structure in Ti-Mo alloys is strongly influenced by the molybdenum content. Thus, the acicular martensitic structure of the α′′ phase is found in Ti-Mo alloys between 3.2% at. Mo and 4.5%, while above a concentration of 4.5 % at. Mo phase ω appears. The appearance of the ω phase leads to an increase in the value of the elasticity modulus, which is why it is undesirable. The study of titanium alloys with an extended ω phase domain is of the future, because in the ω-Ti domain the deformation occurs at the level of cracks and the subject is of interest, related to the effect of plasticity-induced transformations (TRIP) and the mechanisms of plasticity induced by cracks (TWIP). These methods act on the ultra-fine grain that can be produced by high-performance plastic deformation methods (equal channel angular pressing, accumulative bonding, high pressure torsion, etc.) The stable β-Ti phase was identified at a concentration of over 8 % at. Mo. The molybdenum content greatly influences the modulus of elasticity of Ti-Mo alloys. The design of Ti-19Mo-xW alloys by theoretical methods started with the use and combination of the parameters: $\overline{Bo}$ and $\overline{Md}$ [67–73]. The energy level controls the direction of charge transfer, i.e., it is related to electronegativity. The element with higher electronegativity has the lower Md energy level [74]. As electronegativity increases from W to Mo, it follows that electronegativity Md is lower.

The values of $\overline{Bo}$ and $\overline{Md}$ in bcc titanium are:

- for Ti: $\overline{Bo}$ = 2.790, $\overline{Md}$ (eV) = 2.447 (3d);
- for Mo: $\overline{Bo}$ = 3.063, $\overline{Md}$ (EV) = 1.961 (4d); and
- for W: $\overline{Bo}$ = 3.125, $\overline{Md}$ (eV) = 2.072 (5d) [41].

The alloy with higher $\overline{Bo}$ has been shown to have higher corrosion resistance.

One of the aims of the current study is to investigate the alloying effect of Mo and W on the stability of the phase with cvc β-Ti structure.

This time we increased the Mo concentration value to 19%gr. and we varied the concentration of W between 7 and 10%gr. The increase in Mo content (to 19 wt% from the set value of 15 wt%) and its correlation with the increase in W content from 7 to 10 wt% aimed to steer the alloy into the stable beta range. However, the new compositions lead to close values of $\overline{Bo}$ and $\overline{Md}$ ($\overline{Bo}$= 2.82; $\overline{Md}$ = 2.39), as in the case of the previously studied alloys (see map stability phase (Bo)¯and (Md)¯in Fig. 2.2.1.). All are positioned in the stable Ti-beta range, and the data are confirmed by several researchers [2,6,12,64-75]. Alloy design theory is now widely used in obtaining titanium alloys with lower Young's modulus and good corrosion resistance in simulated biological solution (SBF) [75, 76].

The design started by molecular orbital calculation of $\overline{Bo}$ and $\overline{Md}$. The calculated data are in accordance with those of [40] and were correlated with the results of corrosion tests in simulated body fluid (SBF) by linear polarization technique. Tungsten and molybdenum have a high solubility in titanium; the high solubility of molybdenum and tungsten in titanium is due to the similar crystal structure (bcc) and close electronegativity values: Ti - 1.54, Mo - 2.16 and W - 2.36 [26-77]. This is primarily due to the close values of the atomic radius of the elements. The atomic radius values are: Titanium - 0.176 nm, Molybdenum - 0.190 nm and Tungsten - 0.193 nm.

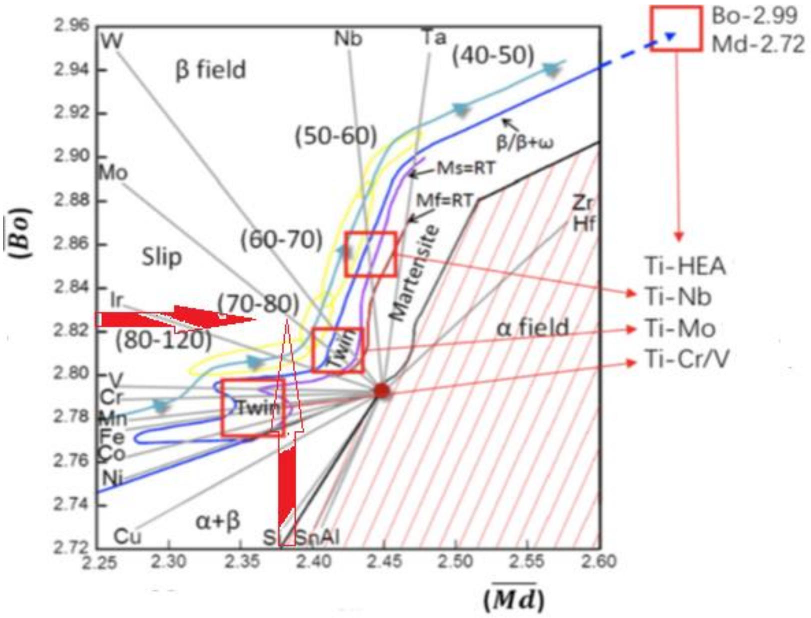

Figure 5.1. Stability phase map $\overline{Bo}$ and $\overline{Md}$, showing the positions of the designed alloys [38, 39]. Recent research has shown that a molybdenum concentration of about 11 % at. Mo (about 19 wt % Mo) concentration chosen for the study of the second β Ti alloy, keeps the elastic modulus values close to the minimum (below 90 GPa).

5.1. Design of Ti-19Mo-xW alloys

The values calculated and presented in Table 5.1.1. positions the obtained alloys in the cvc domain of β - titanium, which can be compared with the values in Fig. 5.1. [22].

Table 5.1.1. Calculated values of $\overline{Bo}$ and $\overline{Md}$ for Ti-19Mo-xW alloys.

	Ti		Mo		W		$\overline{Bo}$	$\overline{Md}$
Code	% gr.	% at.	% gr.	% at.	% gr.	% at.		
1	73,62	86,53	19,21	11,26	7,17	2,19	2,82810851	2,3840165
2	72,5	86,06	19,18	11,36	8,32	2,57	2,8296288	2,38214513
3	71,57	85,61	19,37	11,56	9,06	2,82	2,83101514	2,38023114
4	70,49	85,17	19,22	11,58	10,13	3,23	2,83155687	2,37980337

Along with the increase in the content of tungsten in the investigated Ti-19Mo-xW alloys, an increase in the $\overline{Bo}$ parameter is observed (from the value of 2.8281 for a content of 7.17% wt. W, to 2.8315 in the case of adding 10 .13 wt % W).

The increase in the value of $\overline{Bo}$ from 2.8281 to 2.8315 makes the stability of the β-Ti phase increase (fig. 5.1.), moving it from the limits of the appearance of the ω phase. A more stable β-Ti phase means an alloy with a low elastic modulus; a higher value of $\overline{Bo}$ shows a lower active corrosion rate.

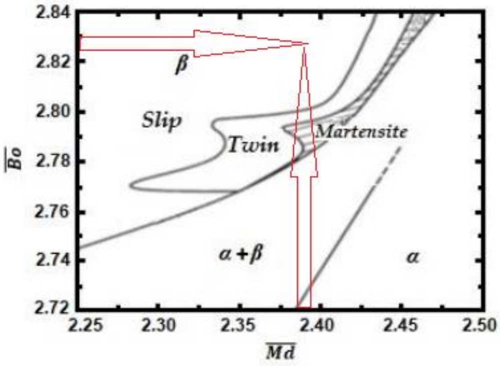

Fig. 5.4.2. Location of the studied Ti-19Mo-xW alloys in the Bo-Md diagram.

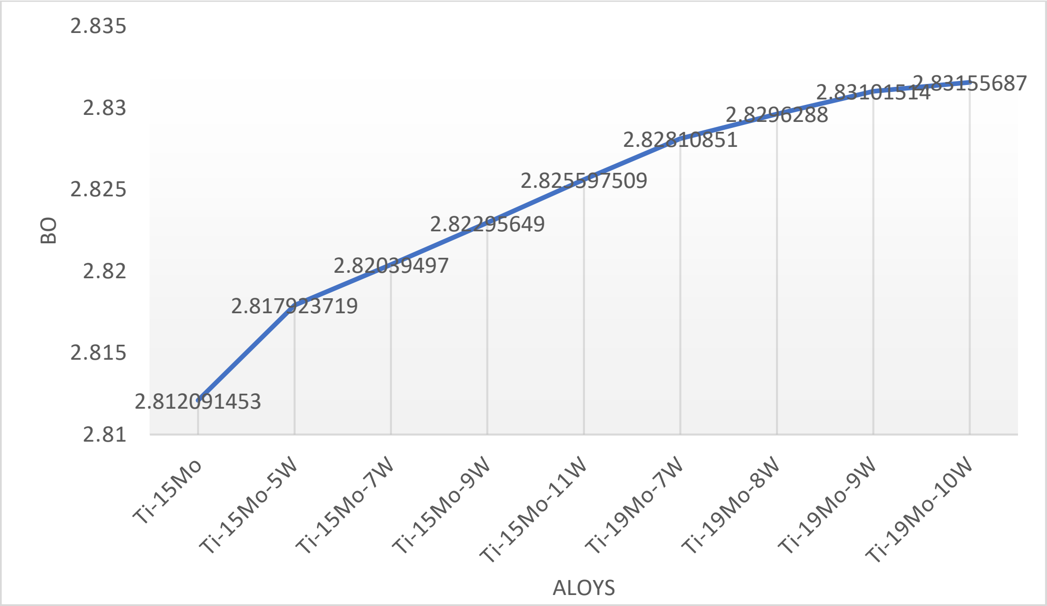

Fig. 5.1.1. $\overline{Bo}$ as a function of tungsten content in Ti-19Mo-xW alloys.

If the value of $\overline{Bo}$ increases, the chemical bond between the atoms of the constituent elements of the investigated alloy becomes stronger, and as the electronegativity increases, the value of the parameter $\overline{Md}$ decreases. Bond strengths correlate with electronegativity difference. These results are consistent with those of other authors [22] and shown in Figure 5.1, demonstrating that the alloys obtained are in the stability region of the β-Ti phase.

In the graph in Fig. 5.1.1. is presented in the same graph, both the evolution of $\overline{Bo}$ depending on the tungsten content in Ti-15Mo-xW alloys, and the evolution of $\overline{Bo}$ depending on the tungsten content in Ti-19Mo-xW alloys; it was found that the evolution is similar.

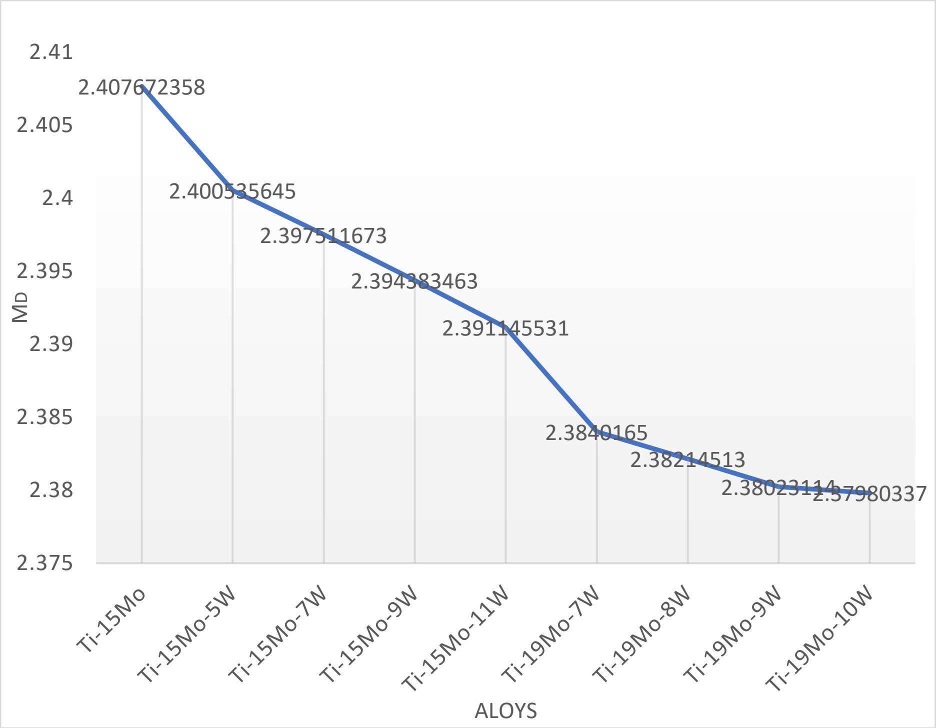

Fig. 5.1.2. Evolution of the $\overline{Md}$ parameter depending on the tungsten content in the Ti-19Mo-xW alloys.

In the graph in Fig. 5.1.2. is also presented in the same graph, both the evolution of $\overline{Md}$ depending on the tungsten content in Ti-15Mo-xW alloys, and the evolution of $\overline{Md}$ depending on the tungsten content in Ti-19Mo-xW alloys; the graph demonstrates that as the tungsten content increases in the composition of the Ti-19Mo-xW alloys, the value of the parameter $\overline{Md}$ decreases.

The ratio of valence electrons (e/a) was calculated according to the electronic configuration of the constituent elements multiplied by the atomic concentration of each element.

$$\frac{e}{a} = \sum_{i=1}^{n} x_i \cdot e_i = x_{Ti} \cdot 4 + x_{Mo} \cdot 6 + x_W \cdot 6$$

x_i = % at. of element *i*;

e_i = valence electrons of element *i*

Electronic configuration for Ti: $1s^2 2s^2 p^6 3s^2 p^6 4s^2 3d^2$ s+d=2+2=**4**

Electron configuration for Mo: $1s^2 2s^2 p^6 3s^2 p^6 4s^2 3d^{10} 4p^6 5s^2 4d^4$ s+d=2+4=**6**

Electron configuration for W: $1s^2 2s^2 p^6 3s^2 p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 5d^4$ s+d=2+4=**6**

In table 5.1.2. the calculated values of the parameter (e/a) for the Ti-19Mo-xW alloy are entered.

Table 5.1.2. Calculated values of the parameter (e/a) for the Ti-19Mo-xW alloy.

	Ţi		Mo		W		$\frac{e}{a}$
Code	% gr.	% at.	% gr.	% at.	% gr.	% at.	
Ti19M7W	73,62	86,539222	19,21	11,266293	7,17	2,194485	4,26921548
Ti19M8W	72,5	86,068008	19,18	11,360275	8,32	2,571717	4,27863984
Ti19M9W	71,57	85,617027	19,37	11,560996	9,06	2,821977	4,28765946
Ti19M10W	70,49	85,175433	19,22	11,587152	10,13	3,237415	4,29649134

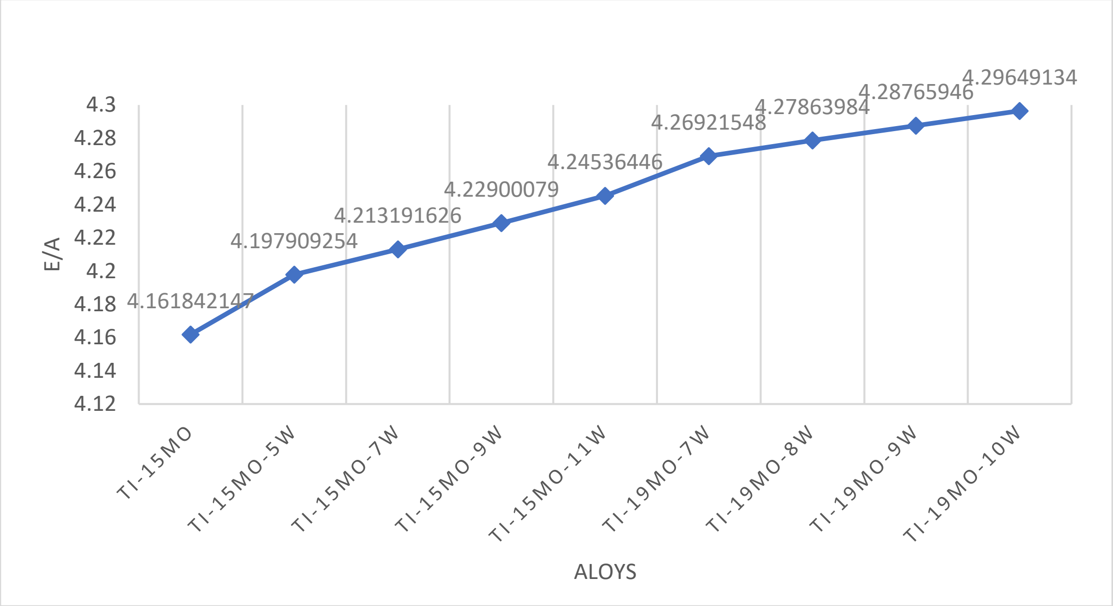

Fig. 5.1.3. The evolution of the parameter (e/a) depending on the tungsten content in Ti-19Mo-xW alloys.

The values (e/a) between 4.26921548 and 4.29649134, above the limit of 4.15 required for the stabilization of the β-Ti phase, position the Ti-19Mo-xW alloys in the field of sliding deformation, due to dislocations (typical of cvc alloys, β-Ti).

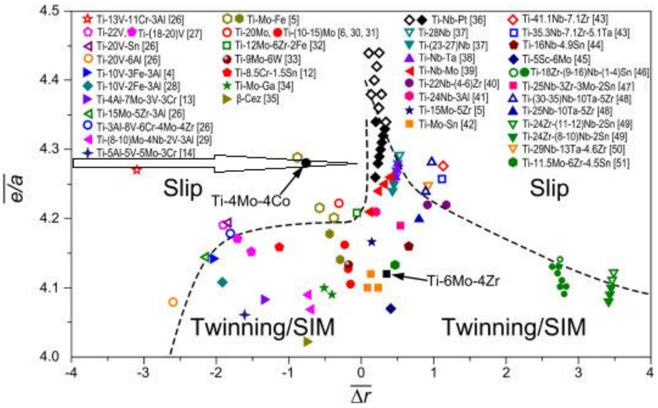

Fig. 5.1.4. Positioning of Ti-19Mo-xW alloys on the $\overline{e/a}$ - $\overline{\Delta r}$ diagram for delineating plastic deformation mechanisms for different β-Ti alloy families.

Obviously, the critical lower limit for stabilization of the β phase which has the value $(Mo_{eq})_Q$ = 6.25 at. pct or 11.8 wt% Mo is far exceeded; $(Mo_{eq})_Q$ for Ti-19Mo-xW alloys is between 22.213 and 23.91.

5.2. Development of Ti-19Mo-xW alloys

The materials used to obtain Ti-19Mo-xW (x = 7, 8, 9 and 10% by weight) were as follows: Commercial purity titanium –Ti grade 1 (ASTM B265 G1), commercial purity molybdenum (ASTM B467). -GrMo-1) and tungsten W1 of commercial purity (ASTM B348 113 GrW1) in wire form φ 0.5 mm.

Table 5.2.2. Chemical analysis of the obtained Ti-19Mo-xW alloys [23].

Code	Aloy	Chemical analizes, % gr.				
		W	**Mo**	**Al**	**V**	**Ti**
1	Ti19Mo7W	7,17	19,21	-	-	73,62
2	Ti19Mo8W	8,32	19,18	-	-	72,50
3	Ti19Mo9W	9,06	19,37	-	-	71,57
4	Ti19Mo10W	10,13	19,24	-	-	70,63
5	Ti6Al4V	-	-	5,92	4,27	89,81

5.3. Characterization of Ti-19Mo-xW alloys

The grain size is about 2 mm. The alloys were also investigated by scanning electron microscopy (SEM-EDS) (Figures 5.3.3 to 5.3.6), and for two samples (Code 1 - Ti19Mo7W and Code 4 - Ti19Mo10W) a BSED analysis (Figures 5.3.7. and 5.3.8.).

It can be seen that there is a uniform distribution of alloying elements, molybdenum and tungsten in the titanium matrix after successive melts, as indicated by BSED mapping and SEI image for Ti19Mo7W alloy in Figure 5.3.7 and for Ti19Mo10W alloy in Figure 5.3. 8.

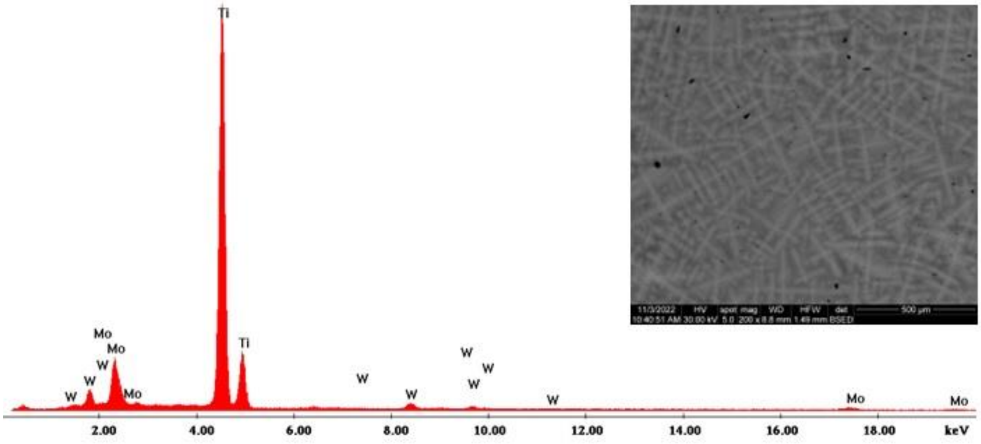

Figure 5.3.3. SEM – EDS analysis for Ti19Mo7W alloy (Code 1)

Table 5.3.1. Chemical composition of Ti19Mo7W alloy (Code 1) (average of local EDX analyses).

	Chemical analizes % gr.			
Element	Edx 1 (Code 1)	Edx 2 (Code 1)	Edx 3 (Code 1)	Media (Code 1)
Titan	73,41	74,05	73,39	**73,62**
Molibden	19,28	18,97	19,38	**19,21**
Wolfram	7,31	6,98	7,23	**7,17**

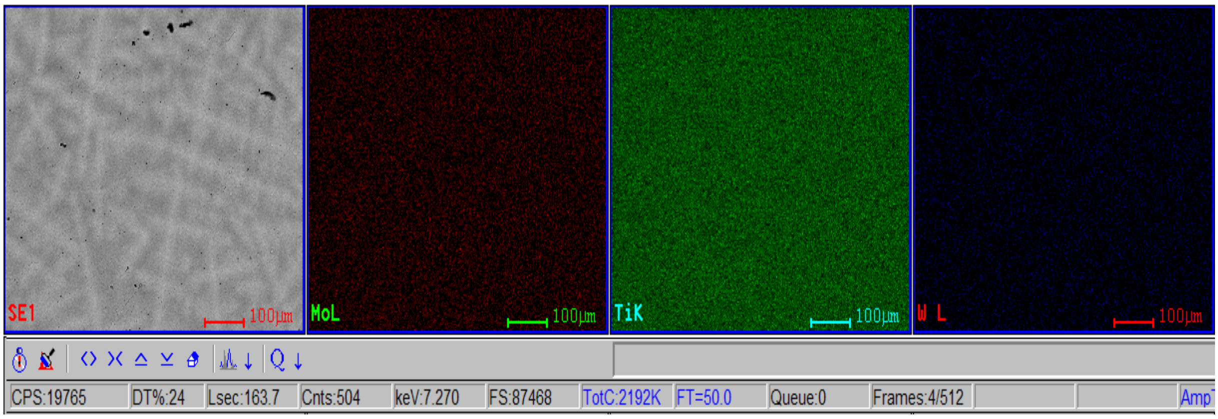

Fig. 5.3.7. SEI image and distribution mapping of W, Mo, and Ti elements (BSED analysis) for Ti19Mo7W alloy (Code 1).

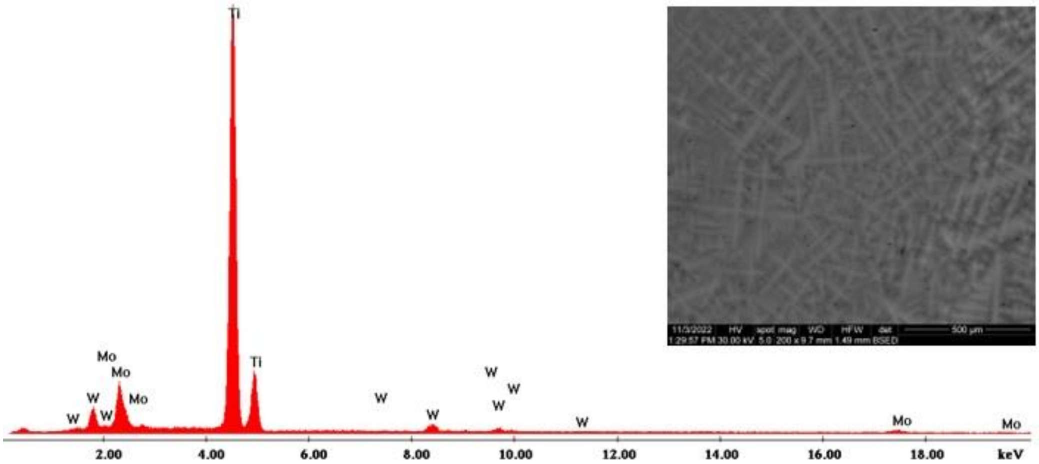

Fig. 5.3.4. SEM – EDS analysis for Ti19Mo8W alloy (Code 2)

Table 5.3.2. Chemical composition of Ti19Mo8W alloy (Code2) (average of local EDX analyses).

	Chemical analizes % gr.			
Element	Edx 1 (Code 2)	Edx 2 (Code 2)	Edx 3 (Code 2)	Media (Code 2)
Titan	72,84	72,33	72,32	**72,5**
Molibden	18,87	19,26	19,41	**19,18**
Wolfram	8,29	8,41	8,27	**8,32**

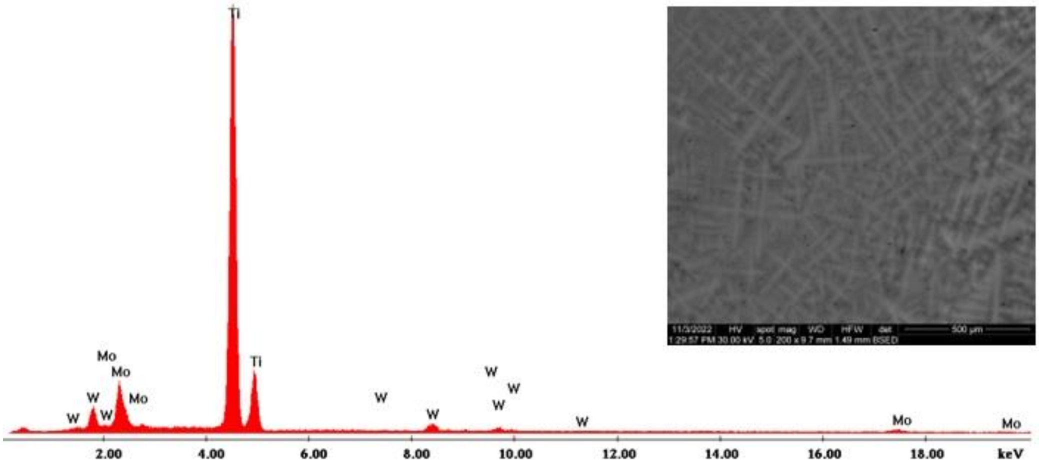

Fig. 5.3.5. SEM – EDS analysis for Ti19Mo9W alloy (Code 3)

Tabelul 5.3.3. Chemical composition of Ti19Mo9W alloy (Code3) (average of local EDX analyses).

	Chemical analizes % gr.			
Element	Edx 1 (Code 3)	Edx 2 (Code 3)	Edx 3 (Code 3)	Media (Code 3)
Titan	71,38	71,31	72,01	**71,57**
Molibden	19,67	19,46	18,98	**19,37**
Wolfram	8,95	9,23	9,02	**9,06**

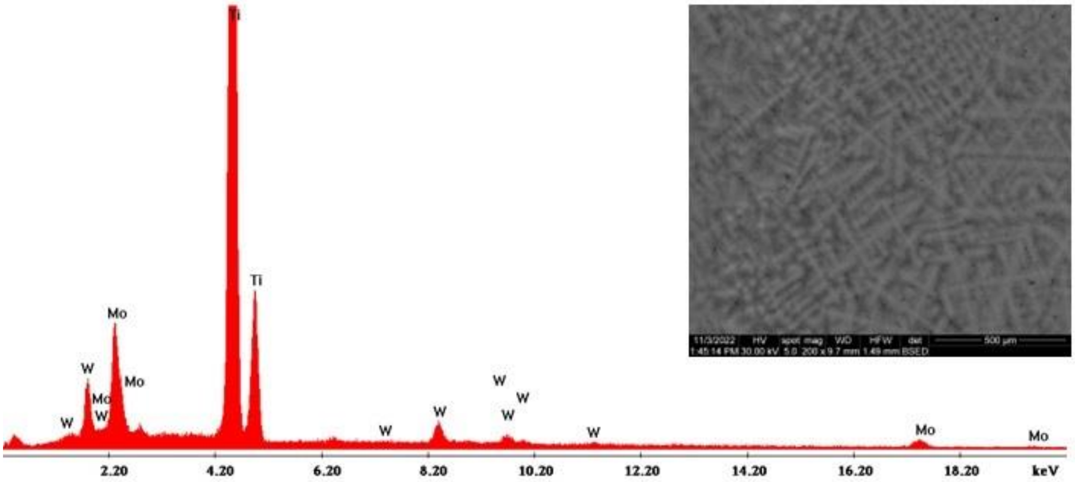

Fig. 5.3.6. SEM – EDS analysis for Ti19Mo10W alloy (Code 4)

Tabelul 5.3.4. Chemical composition of Ti19Mo10W alloy (Code4) (average of local EDX analyses).

	Chemical analizes % gr.			
Element	Edx 1 (Code 4)	Edx 2 (Code 4)	Edx 3 (Code 4)	Media (Code 4)
Titan	71,10			**70,63**
Molibden	19,11	19,52	19,08	**19,24**
Wolfram	9,79	10,42	10,19	**10,13**

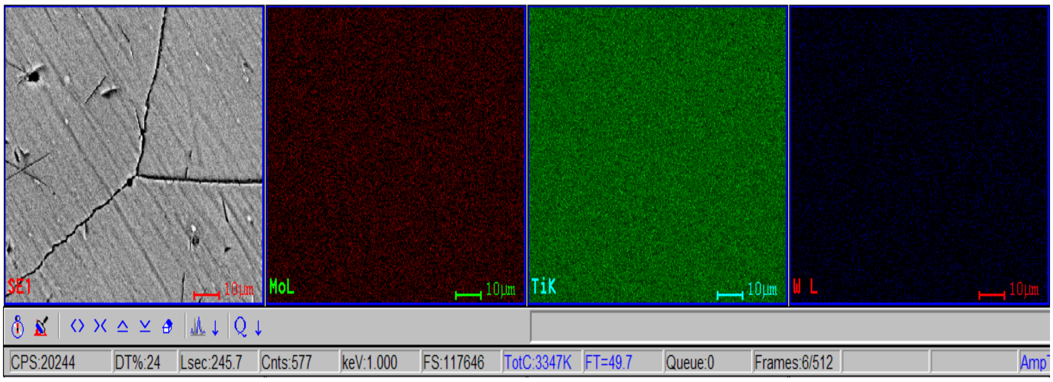

Fig. 5.3.8. SEI image and distribution mapping of W, Mo, and Ti elements (BSED analysis) for Ti19Mo10W alloy (Code 4)

SEM images show the formation of a dendritic structure for all samples obtained. This is also due to the faster cooling of the samples that were melted and kept for solidification in the water-cooled copper crucible. Electron microscopy (SEM and EDS) was used to highlight the uniform distribution of alloying elements after the second melting.

Corrosion resistance in simulated biological solution (SBF)

Corrosion resistance tests were performed using the PARSTAT 4000 (Princeton Applied Research, USA) facility, as seen in Figure 5.3.9. (Left). Electrochemical tests on Ti-19Mo-xW samples (Figure 5.3.9. - right) were performed by linear polarization technique according to ASTM G5–94 (2011) in simulated body fluid solution.

Table 5.3.5. The main electrochemical parameters of the corrosion process in (SBF) of Ti19MoxW alloys [23].

Nr. crt.	**Proba**	**E_{cor} (mV)**	**i_{cor} (nA/cm^2)**	**β_c (mV)**	**β_a (mV)**	**R_p (kΩxcm^2)**	**CR (µm/an)**
1.	1	-331,1	24,214	48,87	557,58	668,69	0,306
2.	2	-282,6	51,987	168,78	101,54	530,22	0,54
3.	3	-293,2	62,584	145,21	148,17	509,48	0,647
4.	4	-272,4	98,861	210,47	227,97	481,28	1,01
5.	Ti6Al4V	-186,2	35,415	118,64	189,75	896,18	0,3220

In terms of corrosion potential (Ecor), a more electropositive Ecor corrosion potential value denotes a more electrochemically "noble" character. Thus, from this perspective, the Ti6Al4V alloy has the highest electropositive value (-186.2 255 mV).

According to literature data, good corrosion resistance is ensured by a low corrosion current density (icor). Taking this criterion into account, we can see that the titanium-based alloy containing 7% W by weight registers the lowest value (29.214 nA/cm2), demonstrating that it has a higher corrosion resistance compared to other investigated alloys. The current densities recorded for the rest of the Ti-based alloys containing 8, 9 and 10 wt% W, have higher values than the reference alloy (Ti6Al4V).

After calculating the corrosion rate (CR) of the alloys following the electrochemical tests performed in SBF, it is observed that the lowest value is obtained for the alloy containing 7% W (0.306 µm/year) followed by the value obtained in the case of the reference sample – Ti6Al4V (0.322 µm/year).

Of these, sample 4 with 10% by weight. W (Figure 5.3.11) shows the highest corrosion rate value, partly because Tungsten is resistant to atmospheric corrosion but reacts at room temperature with halogens (fluorine), and SBF test solutions contain halogens. If the W content increases, the corrosion rate will also be higher.

Another cause is the method of obtaining Ti-Mo-W alloys by melting in the electric arc furnace, which does not provide a good distribution of tungsten in the alloy, appearing areas with agglomerations (Figure 11 - left). To limit this impediment, the use of other methods of obtaining alloys (mechanical alloying and sintering) is tried [26].

For the accumulation shown in Figure 5.3.10, EDX analysis was performed, which highlights the presence of tungsten (fig. 5.3.11).

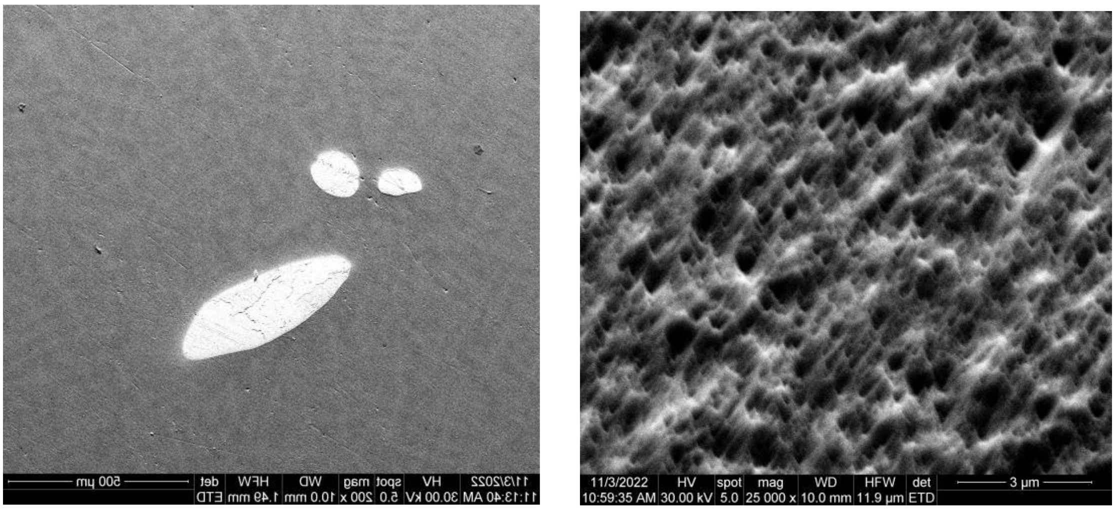

Figure 5.3.10. SEM images of a micro-area showing tungsten accumulation (left) and heavily corroded area (right) of Ti19Mo10W alloy (Code 4).

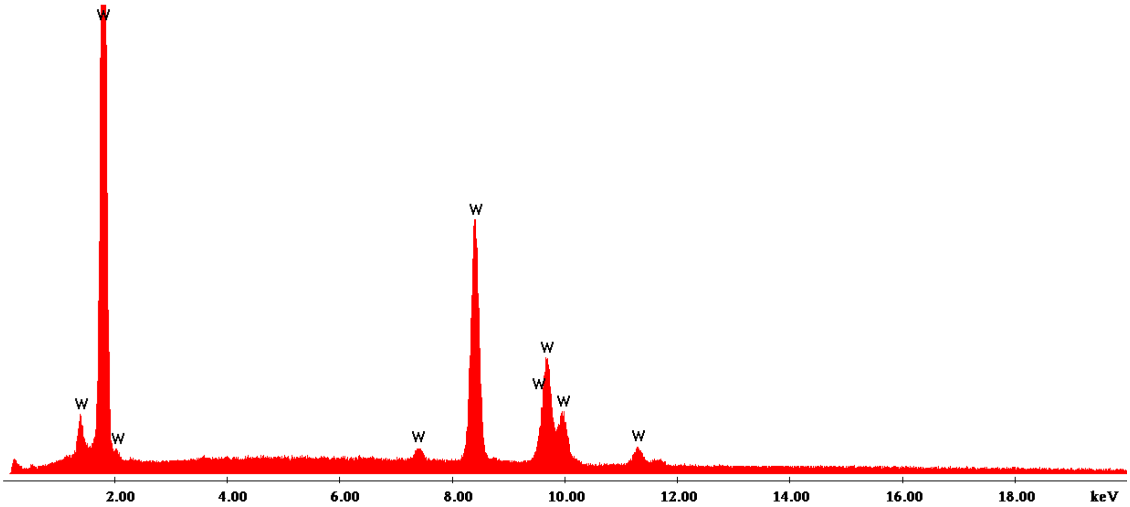

Figure 5.3.11. EDS characterization of micro-zone showing tungsten accumulation in Ti19Mo10W 283 alloy (Code 4).

Based on the results obtained from the polarization curve and the electrochemical parameters of the corrosion process, the Ti-19Mo-xW alloys were found to be corrosion resistant.

Table 5.3.5 presents the main electrochemical parameters obtained from the corrosion tests carried out in SBF.

Figure 5.3.12 shows the correlation between the corrosion rates of the investigated alloys, depending on the values of the parameter $\overline{Bo}$.

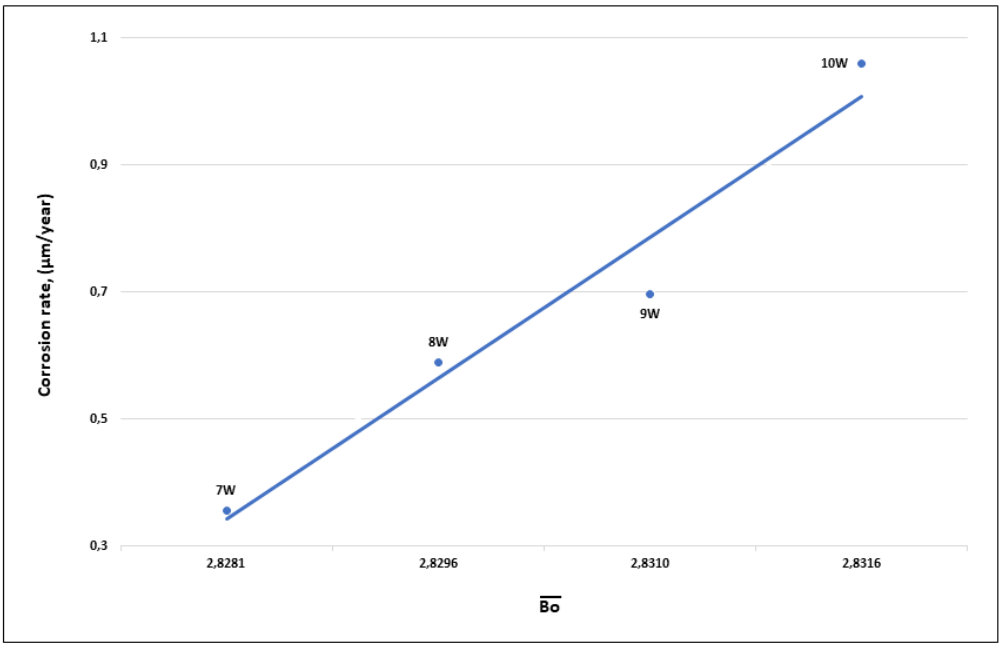

Figure 5.3.12. Correlation of corrosion rate, CR (µm/yr) with Bo for Ti-19Mo-xW beta alloys.

Better corrosion behavior of a material is evidenced by high polarization resistance (Rp). Thus, all 4 Ti alloys have lower values than the value of the reference alloy. Among these, the Ti19Mo7W alloy stands out with a value of 668.69 kΩxcm^2.

Comparing the values of the electrochemical parameters corresponding to the investigated alloys from the point of view of corrosion resistance in SBF, it can be concluded that the alloy Ti19Mo7W (Code 1) stands out for the lowest value of the corrosion current density and the lowest corrosion speed.

PART III - FINAL CONCLUSIONS, ORIGINAL CONTRIBUTIONS, DIRECTIONS FOR FURTHER RESEARCH

Chapter 6.1. Final conclusions

The studies and research undertaken for this PhD thesis focused on the design, development and testing of new biocompatible β-Ti alloys.

Analyzing the three types of materials used in medicine - stainless steel, Co-Cr alloys and titanium and titanium alloys, we believe that each of these materials fulfills certain unique conditions that make them irreplaceable. Titanium alloys cover the widest spectrum of applications in medicine, but its use still presents risks. The Ti6Al4V alloy (with α+β structure) considered today as a standard, presents a health risk due to the release of toxic Al and V ions that can cause cytotoxicity. β-Ti alloys are on the way to replace, if not immediately, then in the not too distant future the titanium alloys with the α+β structure.

The approach to designing β-Ti alloys is bold and opens up many opportunities by reducing research time and related expenses.

The alloy design data put into practice in the thesis were confirmed by a large number of analyses.

The conclusions drawn from the design, development and testing of **Ti-15Mo-xW** alloys are numerous:

The design of the alloys by the molecular orbital method was carried out based on the four essential parameters: Bo, Md, e/a and Moechiv;

Analyzing the evolution of the Bo parameter according to the composition of the Ti15MoxW alloys, it was found that its value increases with the concentration of W from the value of 2.812 (To15Mo) to 2.8179 (To15Mo5W), reaching 2.82558 (To15Mo11W). From the extended diagram (Bo)¯-(Md)¯(fig.2.2.1.) it can be seen that this fact stabilizes the β-Ti phase, moving the position of the studied alloys away from the limit of appearance of the ω-Ti phase.

The maximum value of (Bo)¯of 2.82559 is reached in the case of the To15Mo11W alloy, it is located far below the value of (Bo)¯of 2.84, the limit value established by Morinaga [80-87] for the appearance of the ω-Ti phase;

The evolution of the parameter (Md)¯(the energy level of the d orbital) as a function of the concentration of W, in the case of the studied To15MoxW alloys, confirmed that there is a shift to the left, in the zone of stability of the β-Ti phase and exclusion of the ω-Ti phase, of the parameter (Md,)¯ from 2.4076 (for the To15Mo alloy) to 2.3914 (To15Mo11W) with the increase in the content of W in the alloy;

The evolution of the displacement of the studied alloys on the extended diagram (Bo)¯-(Md)¯ (fig.2.2.1.), is also favorable from the point of view of the evolution of corrosion. Morinaga and X.H. Min, independently concluded that the corrosion resistance increases linearly in the case of (Bo)¯from the value of 2.7900 to 2.823 in Ti-Mo alloys. Research on the corrosion of To15MoxW alloys, both in artificial saliva (SA) and in SBF, established that the icor (nA/cm2) values that have a decisive role in determining the corrosion values have acceptable values in both considered environments (of the order of tens of nA/cm^2). These values show that the studied alloys do not require additional surface protection.

Regarding the e/a parameter (valence electron ratio) the calculated values and the evolution of the e/a ratio depending on the tungsten concentration, led to the conclusion that starting with a tungsten concentration higher than 7%gr. the e/a ratio varies between 4.2...4.24. According to Mohamed Abdel-Hady (2006), Qing Wang (2015), the e/a concentration must be greater than 4.15, to have a β -Ti domain as stable as possible. X-ray diffraction analysis confirmed that in the studied alloys we only find the β-Ti phase and tungsten carbides (WC, W_2C).

The last parameter analyzed in the design stage of Ti15MoxW alloys was the evolution of molybdenum equivalent (Moeq) as a function of tungsten concentration. From the Ti-Mo equilibrium diagram (Fig. 2.2.5.) it can be seen that the monotectoid point is positioned at 10%at. Mo (21.46%gr.Mo), and in the studied alloys, as the tungsten content increases to 11%gr, Mo_{eq} reaches 19.84, moving away from the α Ti zone.

From the electron microscopy analyzes performed on the Ti15MoxW alloys, it resulted that homogeneous alloys were obtained in the VAR furnace, with a grain size around 1.53 mm. The chemical compositions of the alloys, established by spectral means, were confirmed by point analyzes carried out by electron microscopy methods (EDAX).

Corrosion analyzes in artificial saliva (SA) and in simulated biological solution (SBF) to which the Ti15MoxW alloys were subjected, were compared with the established values of the corrosion resistance of the Ti6Al4V alloy.

Following the corrosion analyzes performed both in artificial saliva (SA) and in simulated biological solution (SBF) - which is more aggressive, to which the Ti15MoxW alloys were subjected, it was observed that, with one exception (sample 2 - Ti15Mo9W), the corrosion parameters are acceptable (icor has values of the order of tens of nA/cm2). In sample 2 Ti15Mo9W, the icor value =105.649 (analysis in SBF) represents an atypical result, due to the presence of a material inhomogeneity – a tungsten particle not dissolved in the metal bath.

These corrosion resistance values are close to those of the Ti6Al4V alloy and confirm that the alloy does not require additional surface protection

The conclusions drawn from the design, development and testing of **Ti-19Mo-xW** alloys are important, given that the research has been extended into a compositional spectrum of great perspective. Some of the conclusions drawn are presented below:

The design, development and research of titanium alloys for medical implants are necessary to understand the corrosion behavior in biological solutions similar to the environment of the human body.

The addition of an additional amount of molybdenum to the alloy is not accidental.

From the design stage, I mentioned that with the increase in molybdenum content towards Ti-20%gr. Mo, the alloy stabilizes in the domain of slip deformation, due to dislocations, thus avoiding the domain of deformation by loops (ω Ti domain).

In addition, even if the Mo content reaches 19 wt%. and that of W reaches 10 wt%, the calculated values of Bo and Md are very close to the values calculated for the previously studied Ti15MoxW (x = 1 to 11) alloys, demonstrating that the alloys now investigated are also in the stable beta range. The Mo/W weight ratio in the studied Ti-Mo-W alloys is kept close to 3.

The high molybdenum concentration of about 11 % at. The Mo (about 19 wt.% Mo) concentration chosen for the study of the second β-Ti alloy was chosen to keep the elastic modulus values close to the minimum (below 90 GPa). The Ti-19Mo-xW alloy system (x = 7, 8, 9, 10 wt.%) was investigated regarding the influence of different tungsten contents on the corrosion behavior in simulated body fluid (SBF) by means of the linear polarization technique and correlations were made with Bo and Md values.

- In the case of Ti-Mo-W alloys, the chemical composition can vary widely even if the Bo and Md values calculated based on the chemical composition are found in the Ti beta ranges.

Extending the range of beta titanium alloys to a chemical composition of Ti-19Mo-xW, it was found that the Mo concentration can be increased up to 19%, only on the condition that the W concentration is also kept at the lower limit of 7% by weight, so that the corrosion rate is minimal.

- As a general conclusion, with the increase of W content from 7 to 10 wt%, the value of Bo increases from 2.8281 to 2.8315 and the value of Y decreases from 5.2121 to 5.2110.

- The corrosion resistance of alloy samples depends on the composition. Based on the results obtained following the corrosion process, the Ti-19Mo-xW alloys prove to be resistant to the stresses they were subjected to.

- Comparing the values of the electrochemical parameters corresponding to the investigated alloys in terms of corrosion resistance in SBF, sample 1 – Ti19Mo7W (where Bo is the smallest - 2.8281) have the lowest values of corrosion current density and corrosion speed.

- Research on the corrosion of To19MoxW alloys, in SBF, established that the icor values (nA/cm2) that have a decisive role in establishing the corrosion values have acceptable values in both considered environments (of the order of tens of nA/cm^2). These values show that the studied alloys do not require additional surface protection.

The final conclusion of the research is that the purpose and objectives of the doctoral thesis were fully fulfilled, the two types of alloys, i.e. alloys of Ti + 15%Mo + W (5-11% gr. W), and alloys with the composition Ti19MoxW, i.e. alloys of Ti + 15%Mo + W (7-10%W), correspond to the requirements for use in implantology.

The design of alloys is an option that must be expanded in the case of other biocompatible alloys and not only (superalloys).

Analyzing the Ti19MoxW type alloys, we noticed that these alloys belong to the family of titanium alloys, which, when properly heat-treated, belong to the group of superplastic alloys.

The domain of the ω-Titanium phase allows the development of deformation processes by cracking (cracking/martensite induced by stress give phase transformations).

β-Ti alloys are promising alloys, which need to be further tested.

Chapter 10.2. Original contributions

The originality of the work consists in the application of the material design theory using the physico-chemical properties of the component elements of the alloy (Bo - electronic parameter considering the characterization of the strength of the covalent bond between Ti and the alloying elements (bond order); Md - the energy level of the d orbital, electronic parameter that characterizes the orbital energy d, with reference to the radius and electronegativity of the elements; the ratio of valence electrons e/a; the equivalent in Molybdenum of the elements added to the titanium alloy, Moeq) to obtain new alloys from the β-Titan family.

The alloys were designed in such a way that they meet strict conditions regarding the structure (to be in the β-Titanium range), mechanical characteristics (strength, low elastic modulus), corrosion resistance in artificial saliva environment and simulated biological solution).

After processing, in an electric vacuum arc furnace, the two alloys: alloys with the composition Ti15MoxW, i.e. alloys of Ti + 15%Mo + W (5-11% wt. W), and alloys with the composition Ti19MoxW, i.e. Ti alloys + 15%Mo + W (7-10%W), were subjected to a package of tests (optical microscopy, electron microscopy, X-ray diffraction, corrosion tests) that confirmed the predictions from the design phase.

The interpretation of the results obtained from the tests (characterization of the alloys, structural, microstructural, by diffraction, corrosion tests) represents another contribution of the author to the development of new biocompatible titanium alloys.

The results obtained from the research were materialized through a number of 4 articles, of which 3 articles were published in journals with an impact factor (2 in Materials (FI=3.4/2023) 1 in the UPB Bulletin Series B (FI-0 ,5/2023), of which 3 as first author.

Chapter 10.3. Directions for further research

The research undertaken although laborious is still limited (the number of batches/samples developed and characterized was small; development was not performed in an electric arc furnace with a consumable electrode recommended for the development of titanium alloys). The samples prepared in this way must be subjected to further testing:

- mechanical testing of Ti15MoxW alloys (Ti+ 15%Mo + W (5-11% gr. W), and of alloys with the composition Ti19MoxW, i.e. alloys of Ti + 15%Mo + W (7-10%W) ;
- fatigue testing of the two types of investigated alloys;

- evaluation of the biocompatibility of Ti15MoxW and Ti19MoxW alloys through in-vitro tests.

Dissemination of results

1 - **Ş.I. Ghica**; C. M. Cotrut; M. Buzatu; I.V. Antoniac; V. Bag; M. Butu; M.I. Petrescu; R. Stefanoiu; E. Ungureanu; G. Jacob; R.N. Ionescu, *In vitro corrosion behavior of Ti-Mo-W alloys in artificial saliva* – IOP Conf. Series: Materials Science and Engineering 572 (2019) 012028, p1-8; DOI: 10.1088/1757-899X572/1/012028;
2 - M. Buzatu; V. Geanta; R. Stefanoiu; M. Butu; M.I. Petrescu; M. Buzatu; **Ş.I. Ghica**; Antoniac; G. Jacob; F. Niculescu; D. F. Mark; and H. Moldovan, *Mathematical modeling for correlation of resistance to compression with the parameters Md, Bo, and e/a, for the design of titanium β alloys developed for medical applications*, U.P.B. Sci. Bull., Series B, (2019) vol. 81, pp. 183 – 192; **IF=0.5;**
3 - M. Buzatu, V. Geanta, R. Ştefănoiu, M. Butu, M.I. Petrescu, M. Buzatu,I. Antoniac, G. Iacob, F. Niculescu, **Ş.I. Ghica**, and H. Moldovan, *Investigations into Ti-15Mo-W alloys developed for medical applications*, **Materials**, (2019), vol.12, pp. 1-10; **IF=3.34**
4 - **Ş.I. Ghica**; C. M. Cotrut; M. Buzatu; V. Bag; V. G. Guess; M.I. Petrescu; G. Jacob; E. Ungureanu; *Evaluation of the corrosion resistance of Ti-Mo-W alloys in simulated body fluid (SBF)* – U.P.B. Sci. Bull. Ser. B, (2022) vol. 84, pp. 189-198; **IF=0.5**;
5 - **Ş.I. Ghica**; V. G. Guess; M.I. Petrescu; G. Jacob; V. Bag; M. Buzatu; E. Ungureanu-*Design of Ti-Mo-W alloys and its correlation with corrosion resistance in simulated body fluid (SBF)* **Materials,** (2023), 16, 2453, p.1-14; **IF=3.748**