Polytechnic University of Bucharest

Doctoral School of Materials Science and Engineering

SUMMARY OF THE DOCTORAL THESIS

Development of new low modulus alloys for biomedical applications.

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Content

Summary

The doctoral thesis "Development of new alloys with low elastic modulus for biomedical applications" has as its main objective the design, elaboration and characterization of titanium alloys with low elastic modulus and antimicrobial activity for medical applications. Following an extensive literature study on titanium alloys for medical implants, the fact remains that Ti-Nb-Zr-Ta alloys are of particular interest for the research of implantable biomaterials. The conclusions of the literature study highlighted three guiding elements, necessary in the process of designing new alloys, namely: the use of non-toxic constituent elements, obtaining a modulus of elasticity as low as possible and improving corrosion behavior and antimicrobial character.

In the design part of the titanium alloys, the mathematical modeling was carried out on the weight of the electronic parameters in relation to the estimated structure. The calculation matrix included the variation of the elements tantalum Ta = (0; 5; 10; 15; 20)% mass and niobium Nb = (9; 10; 11; 12)% mass. One of the important conclusions of the theoretical simulation study was that tantalum has a more pronounced betagenic character than niobium, and changing its concentration generates a structure with a higher β-phase proportion at considerably lower concentration values than niobium . Five experimental Ti-9Nb-8Zr-xTa2Ag alloys (x = 0, 5, 10, 15, 20) were obtained and analyzed in the as-cast condition.

The microstructure, corrosion behavior, mechanical and electrochemical properties of the alloys, their corrosion resistance in 3% NaCl solution, as well as in synthetic biological media of phosphate buffer solution (PBS) and artificial saliva were investigated. The experimental in vitro evaluation of the antimicrobial activity of the studied alloys showed that alloying with 2% Ag can induce intrinsic antibacterial properties. The obtained results revealed that the proportion of β phase increases with increasing tantalum concentration, at the maximum concentration almost 90% proportion of β phase is estimated, and the value of the modulus of elasticity decreases continuously with increasing tantalum content in the alloy from 100GPa at 51 GPa. In addition, excellent corrosion behavior, a low corrosion rate and a high passivation tendency are highlighted. The results reported in this paper allow us to consider that TixTa9Nb8Zr2Ag titanium alloys could be a valid alternative for use in orthopedic surgery, and the level of tantalum can be customized according to the nature of the treated bone and the complexity and difficulty of implant processing, namely hardness necessary optimums.

key words: TNZT alloys, biomaterials, corrosion, mechanical properties

Introduction

The topic addressed is to develop a type of alloy for medical applications, which will identify with the host biological structure. The answer to the activity of studying a vast volume of studies and researches available in the specialized literature, was the development of a type of titanium-based alloy with a low modulus of elasticity for biomedical applications.

Following numerous studies, the emergence of osseointegration problems due to very large differences between the values of the modulus of elasticity of the materials that interact in the case of implants is observed, with negative implications in the subsequent healing.

By developing and then using these Ti alloys with optimal values for the longitudinal modulus of elasticity is essential to prevent the phenomenon of shielding and bone atrophy [72].

In this sense, the possibility of creating devices with porous structures having complex shapes, created on the basis of the improvement of the osseointegration process, of the mechanical properties appropriate to the human bone, as well as the reduction of manufacturing costs, for the production of personalized implantable devices, is aimed at. Moreover, in parallel with reaching these targets, work is also being done to obtain an alloy with increased biocompatibility.

The thesis is structured in two major parts, the first part presenting a brief review of an extensive documentary study, the second part including the author's research, contributions and conclusions.

The first part of the paper includes 2 chapters summarizing the theoretical aspects from the specialized literature on which the paper is based. Chapter 1 is dedicated to the characterization of Titanium, the classification of types and its use, as well as the review of the types of titanium-based alloys with the constituents of interest for the work. This chapter also presents the characteristics regarding toxicity and biocompatibility, but also the mechanical properties (modulus of elasticity), resistance to corrosion and fatigue, highlighting their advantages and disadvantages within the conclusions from the literature study. Chapter 2 reviews the objectives of the thesis, the experimental program and the brief description of the program, the development of the chosen alloy and the equipment used in this endeavor. Also presented are the materials, methods and working method that were the basis of the experimental program, as well as the characterization of the obtained alloys.

The second part includes the author's own research, starting with chapter 3 in which an extensive numerical model is followed that allows the construction of an alloy that satisfies certain requirements such as biofunctionality and high biocompatibility, being a TNTZT type alloy. Using concrete values from specialized literature and going through numerous stages of calculation, the constituent elements of the alloy and their propositions are chosen, based on which, in chapter 4, the experimental program will be carried out. Choosing a calculation matrix, this chapter investigates the morphostructural character of the alloys made, this being an indicator of the degradation of the alloys. Chapter 4 also presents a series of mechanical tests both in accordance with the standards in force, as well as tests in the author's own configurations, and continues with an extensive analysis both macroscopically and with the help of optical and electronic microscopes that allow a thorough investigation of the structure of the proposed alloys. Chapter 5 presents experimental results regarding the evaluation of the influence of the surface condition on the electrochemical behavior of the experimental alloys in various environments. The field of use required the study of alloys regarding the wettable modification depending on the chemical composition, in various contact solutions. In order to establish the antimicrobial activity of the alloys, in vitro experiments were carried out using the diffusion disk method and CMI, and the results were reproduced in chapter 6. Experimental research was also carried out regarding the electrochemical behavior of the alloys in NaCl solution 3 % obtaining results on the corrosion rates, and the presentation of the results is contained in chapter 7. The paper ends with chapter 8, in which the author presents his main conclusions, highlights his personal contributions and proposes research directions.

PART I. CURRENT STATE OF RESEARCH, OBJECTIVES OF THE THESIS

Chapter 1. Current trends in the development of titanium alloys for medical applications.

The titanium element with low density, very good resistance to corrosion and the possibility of being manufactured in structured surfaces, optimized in terms of morphology and porosity for osseointegration, is also recommended for use in the medical field. Titanium and its alloys have already been widely used as implant materials due to their remarkable mechanical characteristics cables and biocompatibility, but Ti-Ni is well-known due to its superelasticity and shape memory properties. The literature highlights the toxic nature of some elements and recommends avoiding their use. At the same time, there is a sustained concern for studying the toxic nature of alloying elements because many combinations of alloys have not passed the test of time. The study highlighted that these problems can be solved, it seems, by the development of a new generation of alloys, which, through the non-toxic content of the constituent elements, also ensure the achievement of a reduced modulus of elasticity. Thus, the new generation of titanium alloys brings attention in particular to the matrix of Ti-Nb-Zr-Ta alloys, developed to alleviate these problems, being found to offer a low modulus of elasticity, in addition to the fact that the elements are proven non-toxic.

Chapter 2. The objectives of the thesis, the development of the experimental plan to achieve the objectives, methods and equipment used in the research

The main goal of the thesis is to obtain a titanium alloy with at least satisfactory mechanochemical biointegration properties, which will ensure safety and a superior quality of life for patients in the long term.

The main objective of the thesis is the design, mathematical modeling, elaboration and characterization of titanium alloys with low elastic modulus and antimicrobial activity for medical applications.

In the design of these alloys, based on the information from the specialized literature, the research started from the following premises:

- obtaining titanium alloys containing non-toxic alloying elements from the Ti-Nb-Zr-Ta system, with low modulus of elasticity, as close as possible to that of human bone and antibacterial character by alloying with elements whose effectiveness is proven;
- the development of designed alloys from the Ti-Nb-Zr-Ta system, which would remove the disadvantages of the currently used metal biomaterials;
- Characterization of the alloys from the morpho-structural and mechanical point of view, the evaluation of the corrosion behavior in biofluids, as well as the evaluation of the antibacterial character.

A specialized software (JMatPro) was used to optimize the chemical composition of the alloy, and mathematical modeling was used to estimate the electronic parameters from the Morinaga [156] Bo and Md model. Using the results obtained from the response surface, a generic composition, TiNbZrTaAg, was established for the experimental alloys in which only the tantalum content was modified. The alloys were developed in a vacuum melting facility, according to the technological scheme shown below figure 2.1:

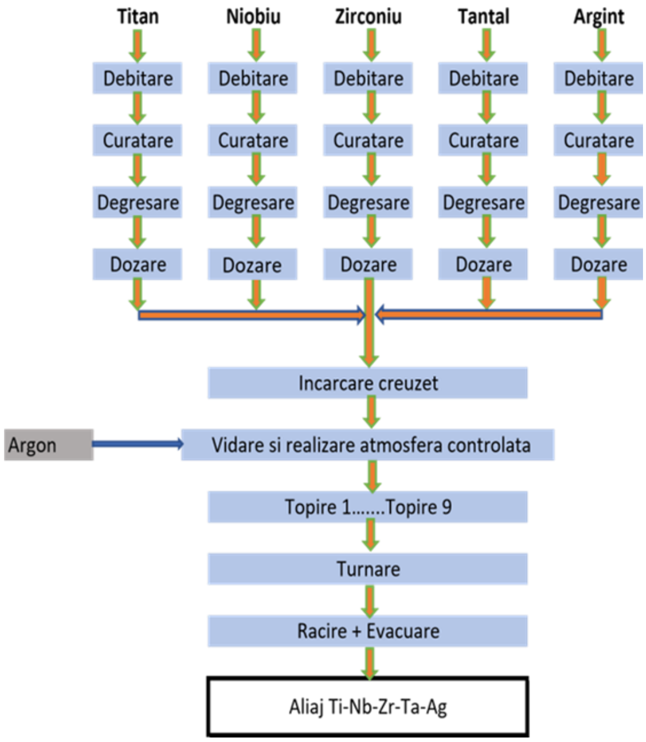


Fig. 2.1 The technological flow of obtaining Ti-Nb-Zr-Ta-Ag alloys

PART II. EXPERIMENTAL RESEARCH, ORIGINAL CONTRIBUTIONS AND CONCLUSIONS

Chapter 3. Alloy design research. Original contributions

3.1 Considerations for choosing materials

In order to obtain an alloy with a reduced modulus of elasticity, comparable to that of human bone, titanium must be alloyed with stabilizing elements of the β phase. There are many elements with a β-stabilizing effect [161], [162] but, to achieve the proposed objective, the elements Ti, Nb, Ta, Zr, considered to be the most biocompatible, were qualified. Silver, a βstabilizing element, but an element with high cytostaticity, still in a reduced proportion in titanium alloys, shows an increased antibacterial effect. [163]

After analyzing the influence of the common alloying elements, the elements Ti, Ta, Nb, Zr can be classified as being very biocompatible. The choice of Ag was made based on the experimental results presented in the specialized literature.

3.2 Design of alloys

In order to achieve the general objective of the thesis, an original methodology was developed which consists of an experiment programmed in several steps to simulate the compositions of the alloys, as follows:

1. Formulation of the main requirements for the realization of a starting composition that presents a β structure, obtaining a low modulus of elasticity, resistance to corrosion in synthetic biofluids and antimicrobial activity.
2. Optimizing the choice of the chemical composition of the alloy, depending on the β phase parameter by means of a specialized software (JmatPro).
3. Development of a software for the calculation of the electronic parameters (Bo and Md) from the Morinaga model, taking into account the element Ag, using Wolfram Mathematica and Microsoft Excel applications.

4. Estimation based on the calculated electronic parameters of the mechanical characteristics for a large number of alloys in the TNZT system.
5. Development of a mathematical model on a matrix of compositions with Ta and Nb elements as variable parameters, to establish the influence of these elements in obtaining the β phase.
6. Optimizing the choice of the chemical composition of the alloys based on the modeled results.

3.2.1 Design method of titanium alloys

The design of the alloy had in mind the concept of creating a composition that would present a β structure, and ensure obtaining a low modulus of elasticity. To achieve this objective, the design was carried out in two stages. The first stage consisted in the computational estimation of the β-phase obtained by simulating several concentrations. The optimization of the choice of the chemical composition of the alloy, to obtain the β phase, was carried out with the help of the specialized software (JMatPro). The results of the estimates are presented in table III.2

Table III.2 The proportion of phases estimated according to %Ta and %Nb

Ta(%) \ Nb(%)	12	11	10	9
20	100%β	100%β	100%β	100%β
15	100%β	100%β	100%β	100%β
10	100%β	100%β	100%β	95.31%β 4.69%α
5	97.51%β 2.49%α	89.53%β 10.47%α	81.54%β 18.46%α	73.51%β 26.49%α
0	76.3%β 23.7%α	68.67%β 31.33%α	61.02%β 38.98%α	53.34%β 46.66%α

Following the simulations, the optimal starting composition Ti68Nb9Zr8Ta15 for the second stage of design through the calculation of the electronic parameters resulted. It was considered that the mass % of the β-stabilizing elements should be as high as possible for safety in obtaining the β phase.

The use of the calculation program provided an approximate information, starting from the design, because the calculation database of the software did not include information about the element silver (Ag). The second phase of the design consisted in completing the data necessary to establish the compositional matrix, based on the calculation of the quantum parameters, the bond order (Bo), the energy level of the d orbital (Md), and the ratio between the valence electrons/atom (e/a) according to the formulas:

$$Md=\sum Md_i x_i \quad \text{Ec. 3.1}$$

$$Bo=\sum Bo_i x_i \quad \text{Ec. 3.2}$$

$$e/a=\sum e_i x_i \quad \text{Ec. 3.3}$$

Where: xi=atomic % of element i; Md_i= bond energy of element i;Bo_i=bond order of element i. The values, calculated based on formulas 3.1-3.3, are presented in table III.3

Table III.3 The values of the electronic parameters Bo, Md, e/a

Aliaj	Bo	Md	e/a
$Ti_{68}Nb_9Zr_8Ta_{15}$	2,89459	2,49649	4,24
$Ti_{66}Nb_9Zr_8Ta_{15}+Ag_2$	2,88067	2,45147	4,18

The analysis based on the diagrams shows that the alloy with silver presents a structure on the border of the β/β+ω phase. To determine the optimal composition, the design includes a mathematical modeling chapter with the aim of assessing the weight of these parameters in relation to the estimated structure. The calculation matrix included the variation of the elements tantalum Ta=(0; 5; 10; 15; 20)% mass and niobium Nb=(9; 10; 11; 12)% mass.

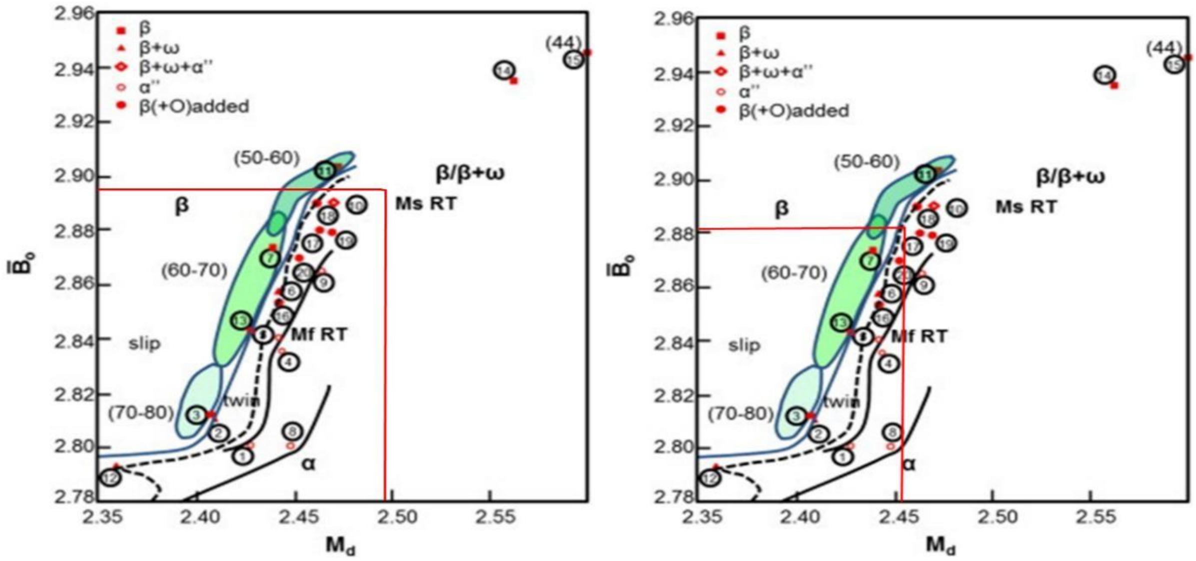


Fig. 3.2 Representation of the alloy position (a) - Ti68Nb9Zr8Ta15; (b) - Ti66Nb9Zr8Ta15Ag2 on the Bo–Md diagram [174]

Plotting the Bo and Md electronic parameters on Morinaga's phase map demonstrates that the use of silver (Ag) as an alloying element acts as a stabilizer of the β phase. The Morinaga method can estimate, in addition to phase formation, values of the elasticity modulus. The influence of alloying with the element silver (Ag) on the Young's Modulus parameter value for the studied alloy, according to the Morinaga principle, is highlighted in Fig. 3.2.

It can be observed that alloying with silver results in the consolidation of the β-type phase, and the increase in the value of the elasticity modulus is quite small, being in the range of (50-60)GPa. It can be said that the presence of Ag as an alloying element ensures the stabilization of the β phase. The antibacterial effect of the addition of Ag represents an important gain in the interaction of the material with the human body, compared to the disadvantage caused by the slight, insignificant increase in the modulus of elasticity.

3.2.2 Mathematical modeling in the design of TNZTA alloys

In the design part of titanium alloys, the first stage considered the titanium-tantalumniobium-zirconium system as a starting point, the advantage of this system, from the point of view of use in medicine, is the presence of alloying elements with a minimal toxic effect or non-existent. The second reason is the fact that, depending on the concentrations of the alloying elements, various structures can be obtained that lead to various mechanical characteristics. The goal of reducing the value of the modulus of elasticity as much as possible

can generate shortcomings in terms of mechanical characteristics of resistance and corrosion, which implies finding an optimal solution by sacrificing some aspects to the detriment of others. Using the model proposed by Morinaga [156] the estimated electronic parameters were the bond order, symbolized by Bo, which represents a measure of the covalent bond between titanium and the alloying element, the second parameter, the energy level of the electron on the "d" orbital , symbolized Md, and a measure correlated with the electronegativity and metallic radius of the elements and the ratio between the valence electrons, symbolized e/a, of the alloying elements. For alloys, the values of Bo and Md are obtained by averaging the values of the individual parameters of the alloying elements. By associating the values of these parameters with a BoMd map indicating the stability of the α, α+β and β phases, a first inference regarding the structure of these alloys is possible.
Through the selection of the main alloying elements, Ti, Ta, Zr and Nb, the options for varying the concentration to induce structural and elastic modulus changes are limited to only two elements, tantalum and niobium, betagenic elements, since zirconium is a neutral element, with a role in hardening.

Using the Bo-Md diagram shown in Fig 3.3, the weight of these parameters in relation to the estimated structure is appreciated. Practically, the weight of the Bo parameter appears to be considerably higher in the migration of the alloy towards a β or predominantly β structure, so the purpose of this optimization becomes the assessment of tantalum and niobium concentrations so as to obtain a maximization of the Bo parameter.

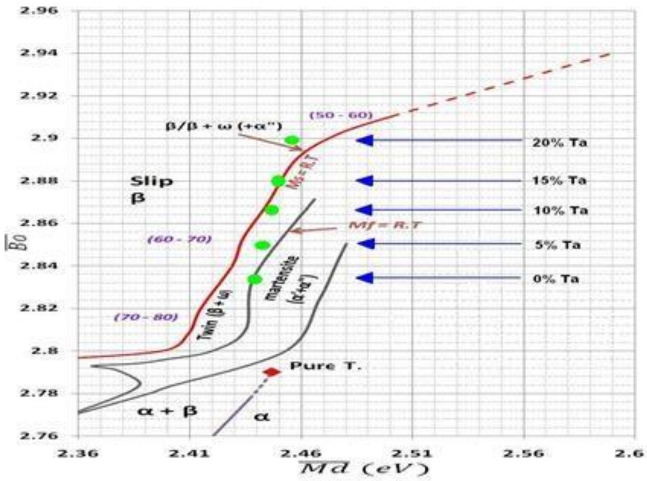


Fig. 3.3 Bo-Md diagram

Based on previous research and the rolled models, the range of concentrations for tantalum (0-20%gr) and niobium (9-12%gr) was narrowed so that the β phase appears in the structure, necessary to effectively control the value of the elasticity modulus.

For this configuration, the values of the electronic parameters of the alloys were determined, as shown in Table III.4 - Table III.6.

Table III.4Bo parameter values the range of selected alloys

Ta(%) \ Nb(%)	12	11	10	9
20	2.90764	2.90455	2.90146	2.89837
15	2.88994	2.88685	2.88376	2.88067
10	2.87224	2.86915	2.86606	2.86297
5	2.85454	2.85145	2.84836	2.84527
0	2.83684	2.83375	2.83066	2.82757

Table III.5 Md parameter values for the range of selected alloys

Ta(%) \ Nb(%)	12	11	10	9
20	2.45078	2.45101	2.45124	2.45147
15	2.45078	2.45101	2.45124	2.45147
10	2.44658	2.44681	2.44704	2.44727
5	2.44238	2.44261	2.44284	2.44307
0	2.43818	2.43841	2.43864	2.43887

Table III.6 Values of the parameter e/a for the range of selected alloys

Ta(%) \ Nb(%)	12	11	10	9
20	4.26	4.25	4.24	4.23
15	4.21	4.2	4.19	4.18
10	4.16	4.15	4.14	4.13
5	4.11	4.1	4.09	4.08
0	4.06	4.05	4.04	4.03

According to the results obtained from the mathematical models regarding the influence of tantalum and niobium concentrations on the structure of titanium-based alloys, it was concluded that tantalum has a more pronounced betagenic character than niobium, and the variation of its concentration would generate a structure with a proportion of β phase higher at considerably lower values than in the case of niobium.

Based on these results, it was decided to keep the niobium concentration constant, choosing the minimum value, 9%, mainly for economic reasons. The alloys used in the experimental program have the estimated chemical compositions indicated in Table III.12

Table III.12 Design compositions for the experimental alloys (%gr)

Aliaj	%Ta	%Nb	%Zr	%Ag	%Ti
A0	0	9	8	2	Rest
A5	5	9	8	2	Rest
A10	10	9	8	2	Rest
A15	15	9	8	2	Rest
A20	20	9	8	2	Rest

The decision to introduce an amount of silver is based on the antimicrobial effect of this element, and previous studies indicate that silver in binary alloys with Ti leads to increased values of mechanical parameters and an improvement in corrosion resistance compared to that of titanium. Also, the studies carried out on the toxicity of the Ti – Ag alloy have shown that it is similar to cp-Ti, an argument previously presented in detail.

For the designed alloys, the estimated structure using the Bo-Md diagram is shown in Figure 3.10

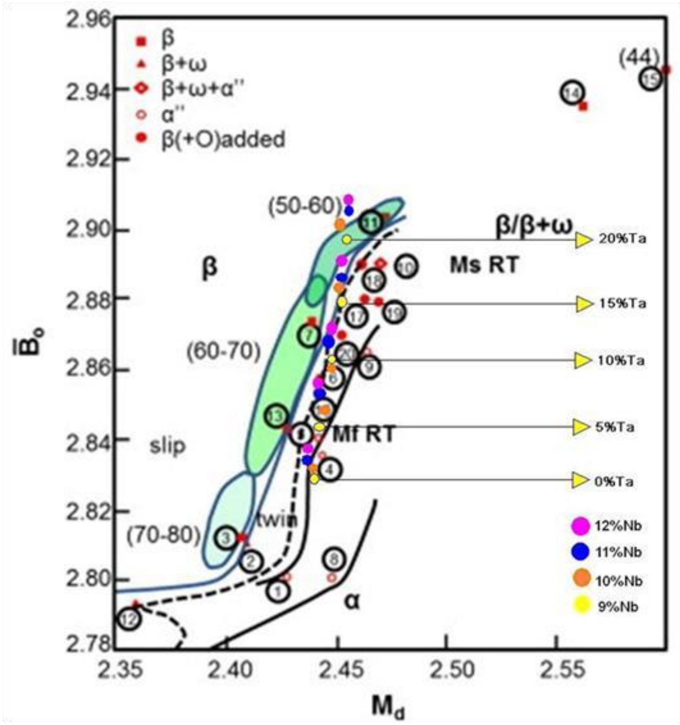


Fig. 3.10 The structure of the experimental alloys on the Bo - Md diagram

The influence of tantalum is evident regarding the stabilization of the β phase, in its absence the structure would be biphasic, α+β, predominating the α phase, the increase in the concentration of tantalum having the effect of an increase in the proportion of the β phase, at 15%Ta the diagram suggests a integral β structure, practically a predominantly β structure is inferred starting from 20%Ta.

In order to analyze the influence of tantalum concentration on the characteristics of these alloys, it was decided to start the experimental program to study the influence of this variable.

3.3 Conclusions

- An original methodology was developed which consists of a programmed experiment in several steps for the simulation/design of alloy compositions.
- Formulation of the main requirements: modulus of elasticity as low as possible, lower than 80GPa and corrosion resistance in synthetic biofluids and antimicrobial activity.
- A software was developed for the calculation of the electronic parameters (Bo and Md) from the Morinaga model using Wolfram Mathematica and Microsoft Excel applications.
- Based on the calculated parameters, the mechanical characteristics of a large number of alloys in the TNZT system were estimated.
- Mathematical modeling and assessment of the weight of these parameters in relation to the estimated structure was carried out. The alloy matrix included the variation of the elements tantalum Ta = (0; 5; 10; 15; 20)% mass and niobium Nb = (9; 10; 11; 12)% mass. • Thus, an equation was established that describes a response surface for each of the three electronic parameters, and the accuracy of the proposed equations was verified.
- The chemical composition of the alloy was optimized with the help of a specialized software (JmatPro) • One of the important conclusions of the theoretical simulation study was that tantalum has a more pronounced betagenic character than niobium, and changing its concentration generates a structure with a higher proportion of β phase, at considerably lower concentration values than in the case niobium.

Chapter 4. Experimental results regarding the development and morphostructural and mechanical characterization of the designed alloys

The method of making these alloys was vacuum arc melting, a process that ensured good homogeneity, due to intense agitation and the elimination of impurities through evaporation, due to the high vacuum (10-6bar).

When loading the crucibles, it was considered placing the materials in the crucible in ascending order of specific weight, so that the melting arc formed ensures the rapid formation of a molten bath of material that includes the elements with increased vaporization tendency.

Table IV.1 Mass quantities of alloy components.

	Determinare masă	Masa(g)				
		Ti	Nb	Zr	Ag	Ta
1	Calculat	98.172	10.908	9.696	2.424	0
	Cântărit	98.176	10.908	9.705	2.422	0
2	Calculat	107.464	12.726	11.312	2.828	7.07
	Cântărit	107.466	12.725	11.309	2.825	7.073
3	Calculat	114.736	14.544	12.928	3.232	16.16
	Cântărit	114.726	14.542	12.929	3.229	16.1603
4	Calculat	106.656	14.544	19.928	3.232	24.24
	Cântărit	106.651	14.55	12.935	3.231	24.26
5	Calculat	86.254	12.726	11.312	2.828	28.28
	Cântărit	86.249	12.721	11.308	2.829	28.286

The development process led to obtaining the five designed alloys, in the form of five ingots with dimensions of Φ 10 mm and L = 140 – 160 mm, shown in figure 4.2.

Fig. 4.2 Image of ingots obtained by melting RAV.

The ingots obtained follow mechanical processing procedures in order to obtain samples and specimens specific to each type of investigation according to the established research plan.

4.3 Experimental results regarding the determination of the density of alloys

The determination of the density of the alloys was carried out using the displaced volume method and the theoretical density was also calculated based on the chemical composition determined by energy dispersive spectroscopy. The composition of the alloys used to estimate the theoretical density is shown in table IV.2

Table IV.2 Chemical composition of the alloys determined by EDX (in weight percent)

Aliaj	%Ta	%Nb	%Zr	%Ag	%Ti
A0	Inexistent	9.15±0.37	8.19±0.23	1.90±0.15	80.76±0.55
A5	3.95±0.30	7.52±0.56	6.87±0.35	1.96±0.08	79.71±1.03
A10	8.94±0.36	10.01±0.71	7.78±0.37	1.95±0.08	71.32±1.02
A15	15.58±0.51	9.32±0.25	7.68±0.23	1.86±0.08	65.55±0.63
A20	19.32±1.31	10.25±2.13	8.56±1.18	2.62±1.19	59.25±3.32

The theoretical density was estimated by the weighted contribution of each element, and figure 4.3 shows the variation of densities, experimentally determined and theoretically estimated, depending on the tantalum concentration.

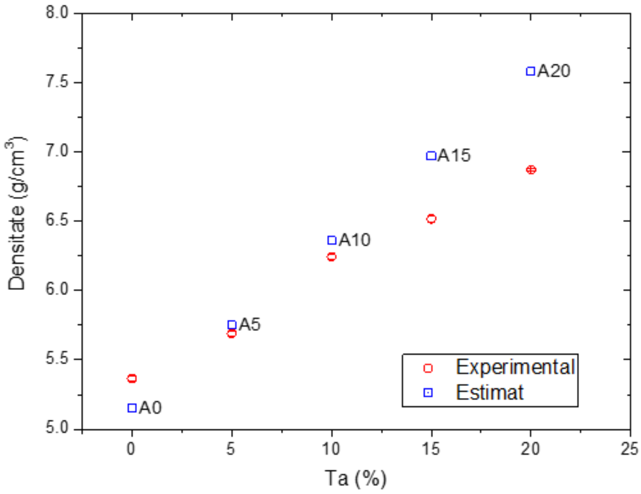


Fig. 4.3 Variation of alloy density according to tantalum content

Determination of proportions of structural constituents

In the case of titanium alloys, the detection of structural constituents is relatively easy through the prism of morphology and color nuances in optical micrographs. For the quantification of the proportions of structural constituents, strictly for the α and β phases, the majority ones, a method was used that uses image analysis performed with the help of the ImageJ software application, a decision made based on the existence of some extensions that greatly facilitate image processing.

In fig. 4.8 shows the variation of alpha and beta phase proportions, depending on the tantalum concentration added to the alloy.

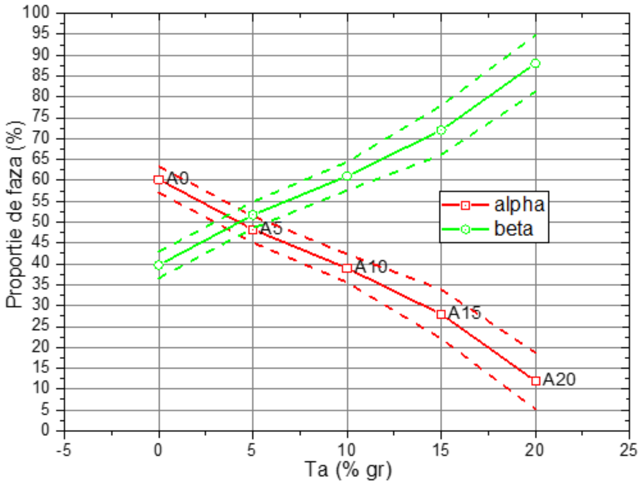


Fig. 4.8 Phase proportions determined as a function of tantalum content

The proportion of β-phase increases with increasing tantalum concentration, at the maximum concentration being estimated to be almost 90% proportion of β-phase, while the alloy without tantalum shows a proportion of about 40% β-phase. Particularly interesting is the fact that the alloy with a content of 5%gr.Ta shows approximately equal proportions of α and β phase.

At a concentration of 20%gr. Your proportion of β phase doubles.

4.4.2 Experimental results regarding the morphostructural characterization by scanning electron microscopy (SEM)

Qualitative assessments

Scanning electron microscopy (SEM) investigations were carried out on each alloy, in several regions, with only a selection of micrographs included in the paper to present the relevant aspects regarding their constituents, morphology and dispersion. Analyzing the constituents, their morphology and distribution in relation to the variation of the tantalum concentration, it is found that the alloys show a Widmanstatten-type morphology up to a content of 10%Ta, later it changes into a morphology consisting of a β-phase matrix with α-phase lamellae in the form of colonies at 15%Ta, and, zonally, with Widmanstatten morphology, while at a content of 20%Ta the α-phase appears as coarse, isolated lamellae in the β-phase mass. At a majority structure consisting of β phase (a tantalum content greater than 15%), the appearance of martensite is inferred, an assumption based on the acicular morphology specific to this constituent outside of equilibrium.

Determination of chemical compositions

Surface and point compositional analyzes were carried out using the SEM-EDX technique. In Fig. 4.14 shows the distribution map of the alloying elements of interest on the investigated surfaces for the experimental alloys.

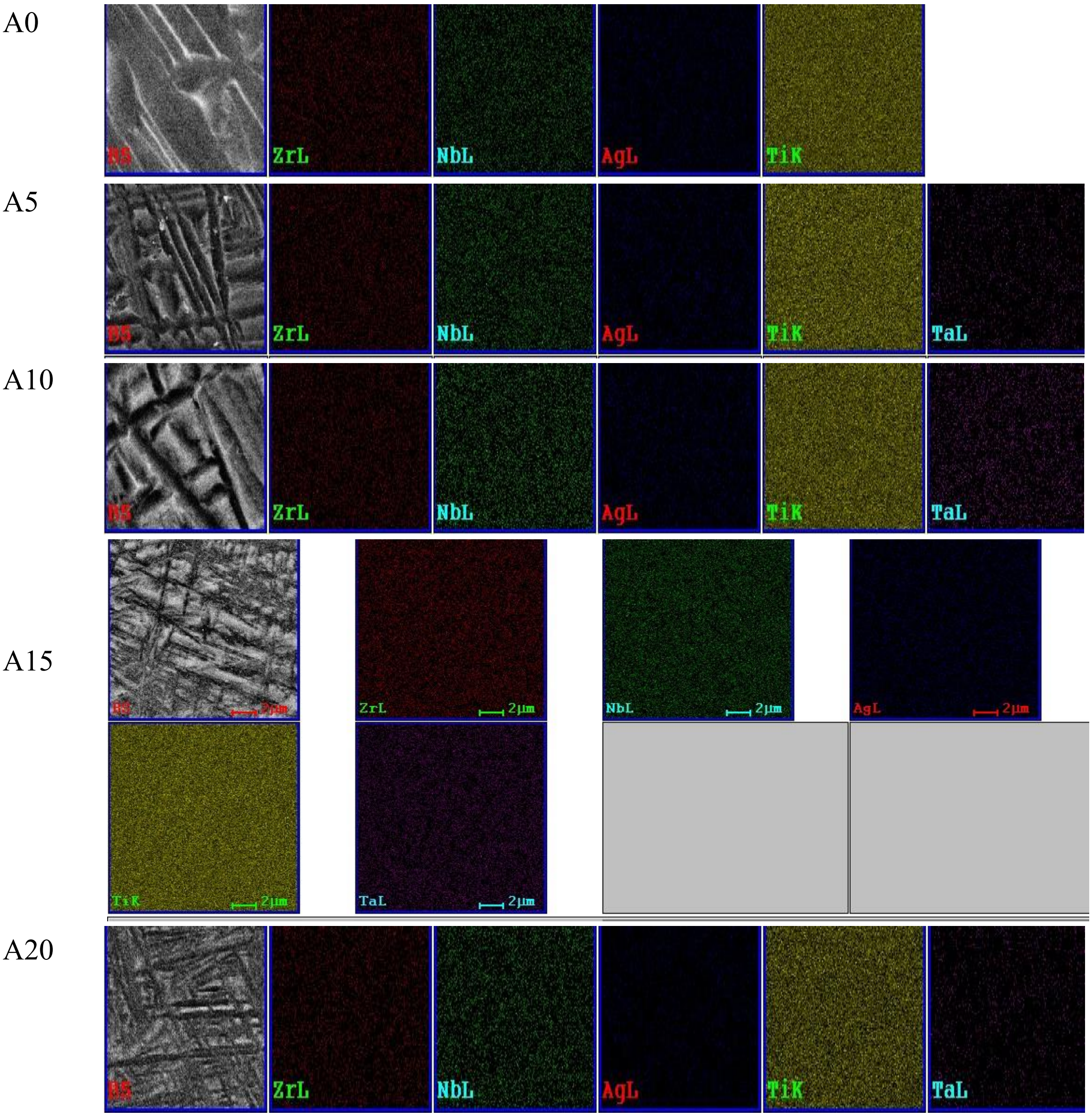


Fig. 4.14 Elemental mapping for experimental alloys

According to the concentration distribution of each investigated alloying element, it can be stated that they present a uniform distribution in the structure, lacking segregations or compounds, the chemical homogeneity being good due to the repeated remelting of the experimental ingots.

As for the chemical compositions, they were estimated based on the EDX spectra obtained following the previous analysis, the mean and standard deviation values, expressed in weight percent, the variation being indicated in Fig. 4.15

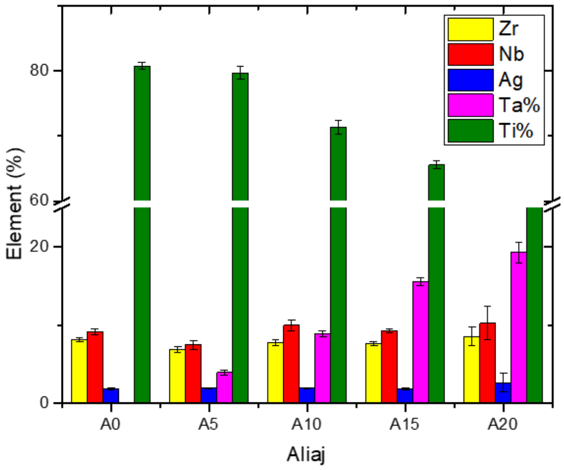


Fig. 4.15 Chemical composition determined by EDX for the experimental alloys

Table IV.3 Chemical composition of the experimental alloys (in % weight)

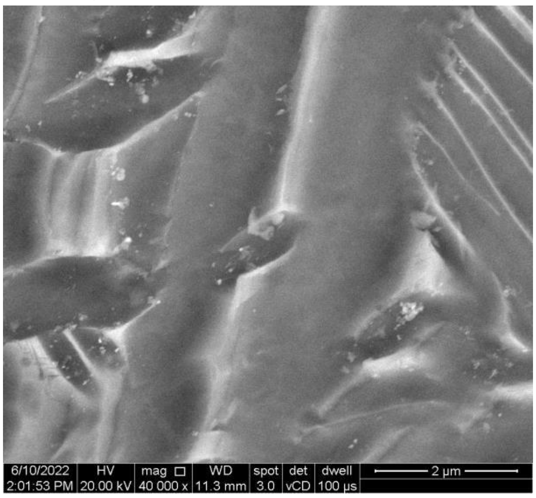
Aliaj	Zr		Nb		Ag		Ta%		Ti%
	medie	abatere	medie	abatere	medie	abatere	medie	abatere	
A0	8.19	0.23	9.15	0.37	1.90	0.15	0.00	0.00	Rest
A5	6.87	0.35	7.52	0.56	1.96	0.08	3.95	0.30	Rest
A10	7.78	0.37	10.01	0.71	1.95	0.08	8.94	0.36	Rest
A15	7.68	0.23	9.32	0.25	1.86	0.08	15.58	0.51	Rest
A20	8.56	1.18	10.25	2.13	2.62	1.19	19.32	1.31	Rest

The obtained chemical composition is considered to be within the compositional tolerances for the proposed experimental program since the concentrations are close to those proposed, within 1-2% by weight.

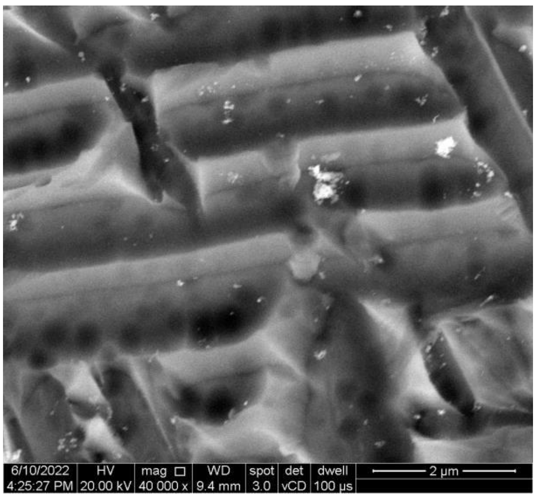
Quantitative structural determinations

The quantitative analysis performed on the micrographs obtained by scanning electron microscopy aims to investigate the stereological parameters of the alloys, in this case the thickness of the α-phase lamellae, using a procedure similar to the one presented and used previously in the optical microscopy investigation.

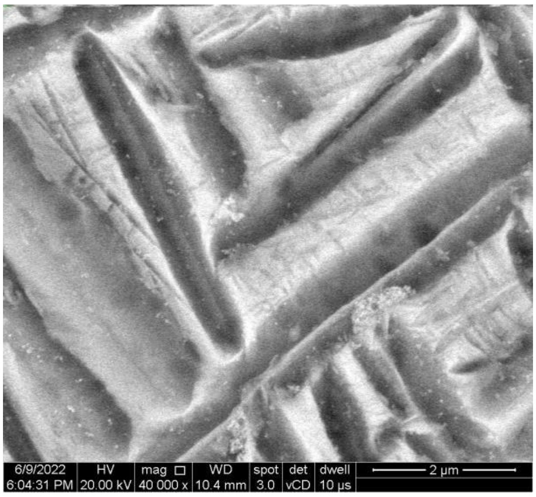
In order to analyze the variation of the lamella thickness, a working methodology was developed using micrographs at high magnifications, to facilitate the measurements, examples of micrographs used are shown in Fig. 4.16.



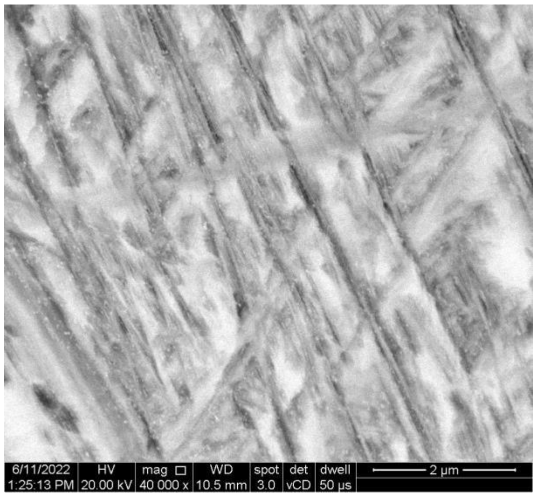
A0



A5



A10



A15

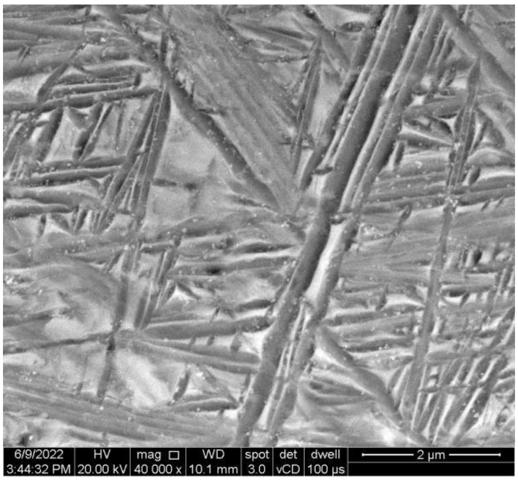


Fig. 4.16 Examples of SEM micrographs used to quantify the lamella thickness of the α phase

A20

In Fig. 4.20 a correlation between tantalum content and lamella thickness is also shown.

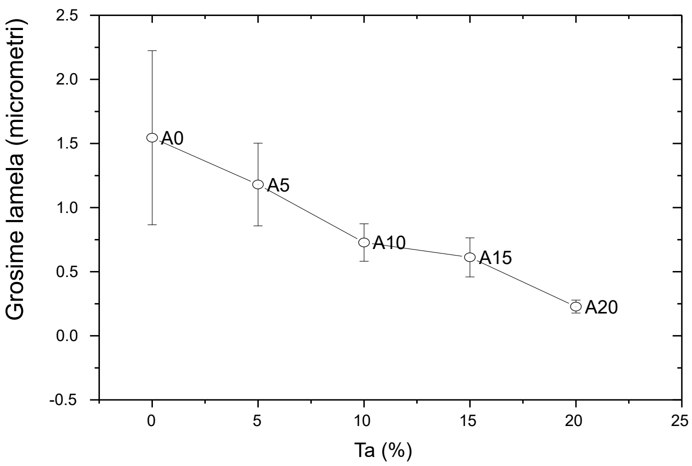


Fig. 4.20 Variation of lamella thickness as a function of tantalum concentration

It is found that with increasing tantalum concentration there is a continuous decrease in the lamella thickness, only the transition from 10-15%Ta would generate equal lamella thickness values

The results of this analysis are in agreement with those obtained by optical microscopy, however some discrepancies are attributed to measurement errors and the reduced resolution of the analysis performed by optical microscopy.

Scanning electron microscopy studies have proven to be relevant for the appreciation, at an intimate level, of the morphology of the structural constituents, for the appreciation of the elemental distribution and the quantification of the chemical composition of the experimental alloys.

4.4.3. Experimental results regarding X-ray diffraction characterization

The main objective of X-ray diffraction analysis was to identify the phases present in the experimental alloys and possibly to quantify the proportions in which they are present. For a quantification and identification of other phases, it is considered to perform the determination using a diffractometer that uses molybdenum as the cathode, not copper as is the case of the one used in the experimental program.

Phase identification and indexing was done using the JCPDS database, from which files 44-1294 for α-titanium and 44-1288 for β-titanium were assigned.

In Fig. 4.21 show the diffractograms of the obtained and indexed experimental alloys. The diffraction maxima coincide with those of the used index sheets, being slightly out of phase to the left of the maximum due to the modification of the lattice parameter due to alloying during the formation of the solid solution.

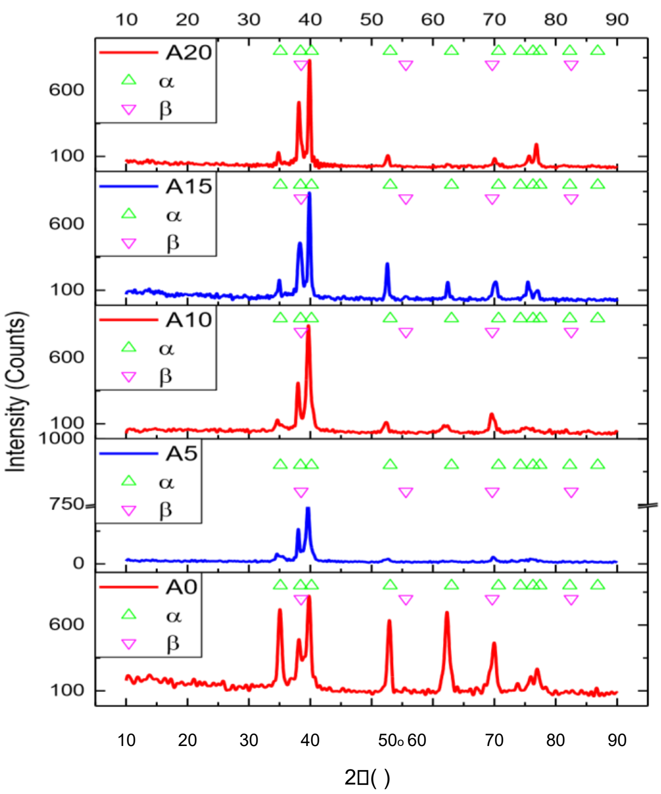


Fig. 4.21 Indexed diffractograms for the experimental alloys

4.4.4. Experimental results on determining the hardness of alloys

The determination of the hardness of the experimental alloys was carried out by the Vickers method, using a stress of 1.961N with a holding time of 15s, complying with the provisions of the ISO 6507-1 standard. The determinations were made in two regions of each ingot, in the central area (symbolized area 1) and a marginal region (symbolized area 2), performing 5 determinations each, the values being averaged. In Fig. 4.24 shows the variation of Vickers hardness as a function of tantalum concentration.

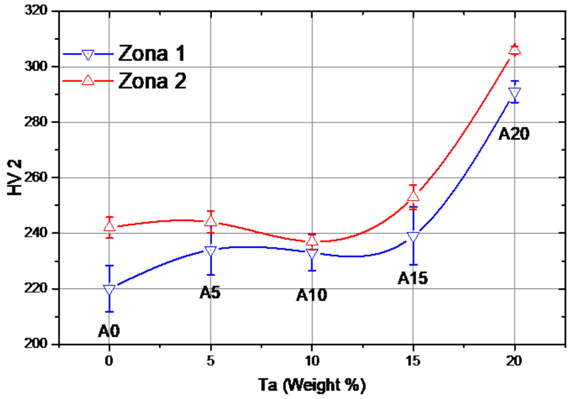


Fig. 4.24 Variation of Vickers hardness as a function of tantalum concentration

An increase in hardness is observed with increasing tantalum concentration, initially a slight increase in hardness up to a concentration of 15%Ta, followed by a spectacular increase (about 70 Vickers units) at 20%Ta. Obviously, there are discrepancies between the central and the marginal zone, the reason being the microstructure variation dictated by the thermal gradient, the marginal zone having a slightly higher hardness. The variation in hardness can also be associated with the proportion of β phase in the alloy, with the increase in the proportion of this phase, the increase in hardness is also found due to the alloying of the solid solution.

4.4.5. Experimental results regarding the mechanical characterization of alloys

The tensile test was carried out according to the specifications of the ISO6892-1 standard, and the ASTM E9 standard was used as a guide for the compression test.

Tensile testing of alloys

The tensile behavior of the experimental alloys can be analyzed through the stress-strain curves shown in Fig. 4.26.

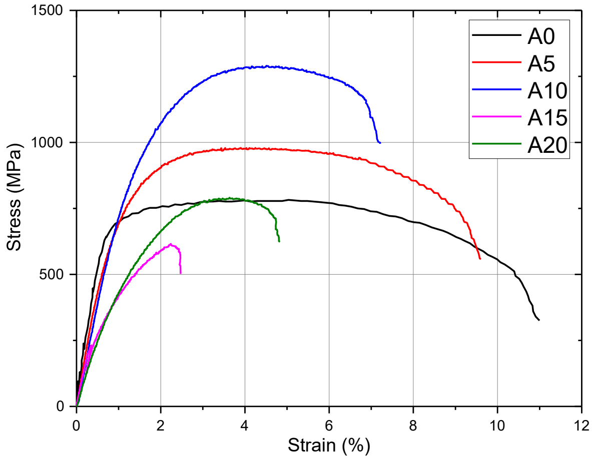


Fig. 4.26 Stress - tensile strain curves for the experimental alloys

Alloy A0 shows the most ductile behavior, showing the highest elongation, followed by alloy A5 and A10. Alloys A15 and A20 show a rather brittle behavior, reduced plastic deformations. Alloys A0, A5 and A10 show a ductile behavior, while alloys A15 and A20 show a brittle behavior, unexpected behavior considering their structure.

Regarding the mechanical characteristics, the modulus of elasticity, yield strength and mechanical strength of these alloys were determined, the elongation at break was considered an unrepresentative parameter mainly due to the structural inhomogeneity of the alloy. In Fig. 4.27

shows the variation of the mechanical characteristics depending on the tantalum concentration in the alloy.

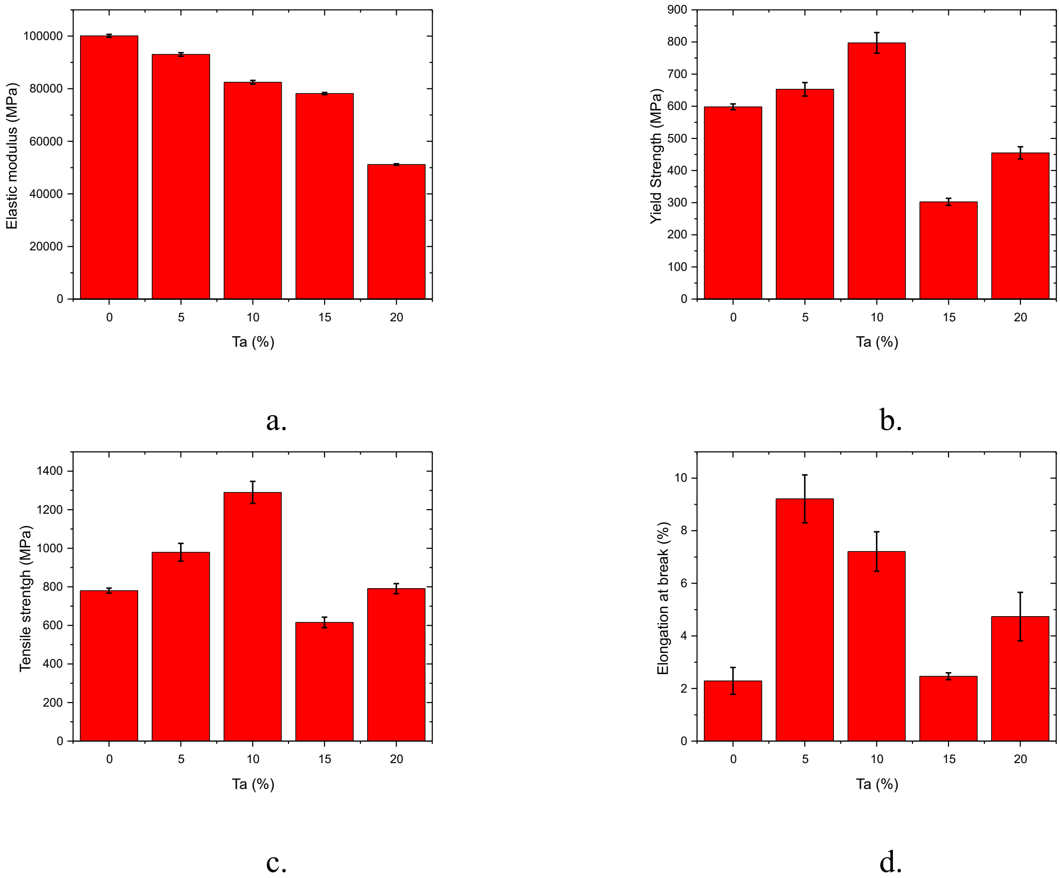


Fig. 4.27 Variation of properties as a function of tantalum concentration, a. modulus of elasticity, b. yield strength, c. mechanical strength and d. elongation at break

Regarding the value of the modulus of elasticity, Fig. 4.27.a, a continuous decrease of it is observed with the increase of the tantalum content. In the case of the A0 alloy, the modulus of elasticity has a value of about 100GPa, 10GPa less than titanium of commercial purity. At 5%Ta the modulus of elasticity decreases to approximately 93GPa, at 10%Ta it reaches 82GPa, at 15% it has a value of 78GPa, and at 20%Ta the lowest value is 51GPa. The influence of tantalum on the modulus of elasticity is obvious, by the considerable decrease - a halving of the value.

The yield strength, mechanical strength and elongation at break are parameters strongly influenced by the microstructure and change accordingly.

Compression test of alloys

The compression test of the alloys was performed until the complete failure of the cylindrical specimens. The compression behavior can be appreciated in Fig. 4.36.

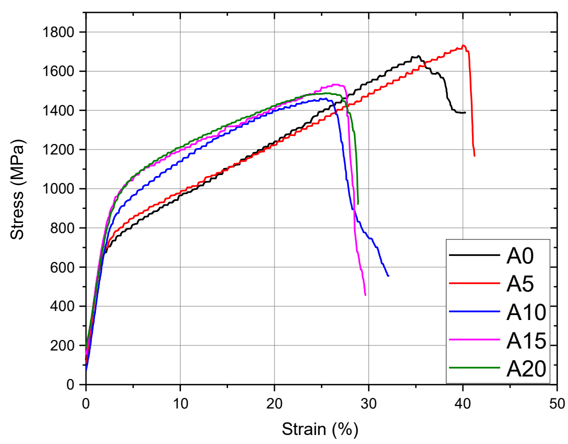


Fig. 4.36 Stress -strain curves in compression for the experimental alloys

4.4.6 Experimental results regarding the tribological characterization of the experimental alloys

For the tribological characterization of Ti alloys alloyed with Ta, two types of tests were performed: pin-on-flat type to determine the coefficient of friction and micro-scratch to determine the scratch hardness.

Experimental results regarding the determination of the friction coefficient

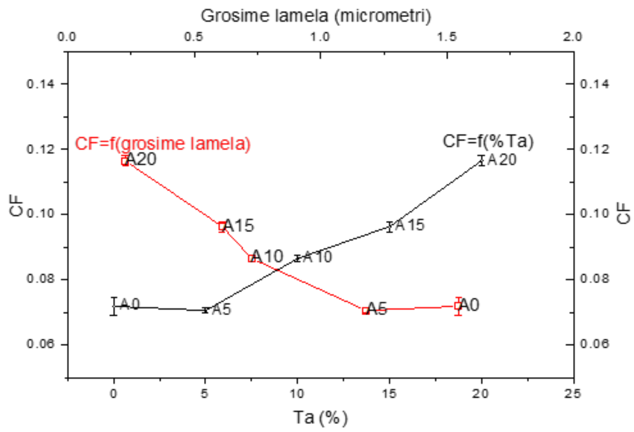


Fig. 4.48 Variation of the friction coefficient as a function of the tantalum concentration and the thickness of the α-phase lamella

Experimental results regarding the determination of micro-scratch resistance

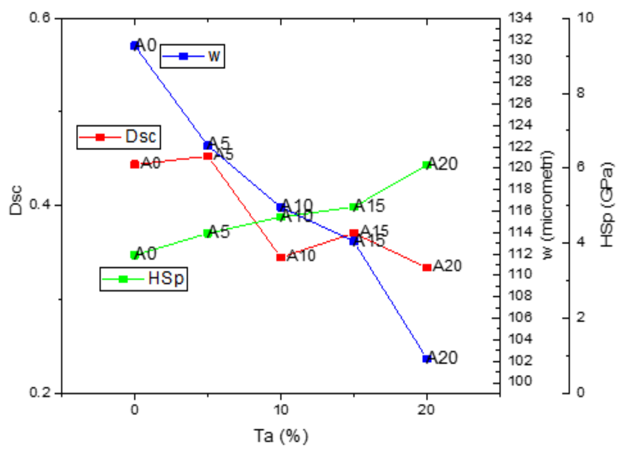


Fig. 4.55 Variation of penetrator resistance coefficient (Dsc), trace width (w) and scratch hardness (HSp) as a function of tantalum concentration

4.5 Partial conclusions

- Scanning electron microscopy studies have proven to be relevant for the appreciation, at an intimate level, of the morphology of the structural constituents, for the appreciation of the elemental distribution and the quantification of the chemical composition of the experimental alloys.
- A work methodology was developed to evaluate the proportion of phases in alloys and the influence of alloying elements: micrographs obtained at magnifications of 5x103, 10x103, 20x103 and 40x103 were used, performing 12 random thickness measurements per magnification, obtaining thus 48 values/alloy. The values were statistically processed, and at the same time the Anderson-Darling test, ANOVA analyzes were performed considering the tantalum concentration as an influencing factor and the lamella thickness as the response, using a significance level of 0.05. Simultaneously, a Tukey test was performed to compare the means.
- The value of the modulus of elasticity decreases continuously with the increase of tantalum content in the alloy from 100GPa to 51GPa.
- In the cast state, these alloys show good mechanical characteristics, but their deformability needs to be remedied by heat treatments.
- Crack initiation at tensile failure of all alloys is type I.
- In the case of the compression test, the microstructure has less influence on the mechanical characteristics than in the case of tensile stress, in the case of compression stress the crack initiation is type II.
- For compressive stresses, the alloy in the cast state presents a stable, easily predictable mechanical behavior, the influence of the structure being much reduced.
- With the increase in tantalum concentration, an increase in the coefficient of friction is observed, inverse variation in the case of lamella thickness: the greater the thickness of the lamella, the higher the coefficient of friction.
- Scratch hardness shows an increasing trend with increasing tantalum content, for alloy A0 its value is 3.6GPa, and at a content of 20%Ta a value of 6.09Gpa is reached.

Chapter 5. Experimental results regarding the evaluation of the influence of the surface state on the electrochemical behavior of the experimental alloys in synthetic biological environments

The state of the surface has a major role in the success of using a material in surgical implantology, through at least two characteristics: roughness and hydrophilicity. Phosphate buffer solution (PBS) and artificial saliva were used as synthetic biological media to characterize the behavior of the developed titanium-based alloys; the tests were performed at a temperature of 37°C by the technique of stationary immersion for 1000 hours coupled with EIS and the Tafel curve method.

To analyze the influence of roughness on the behavior of titanium and tantalum-based alloys in contact with synthetic biofluid (PBS), two of the developed alloys, with different concentrations of tantalum, were selected: Ti20Ta9Nb8Zr2Ag and Ti10Ta9Nb8Zr2Ag.

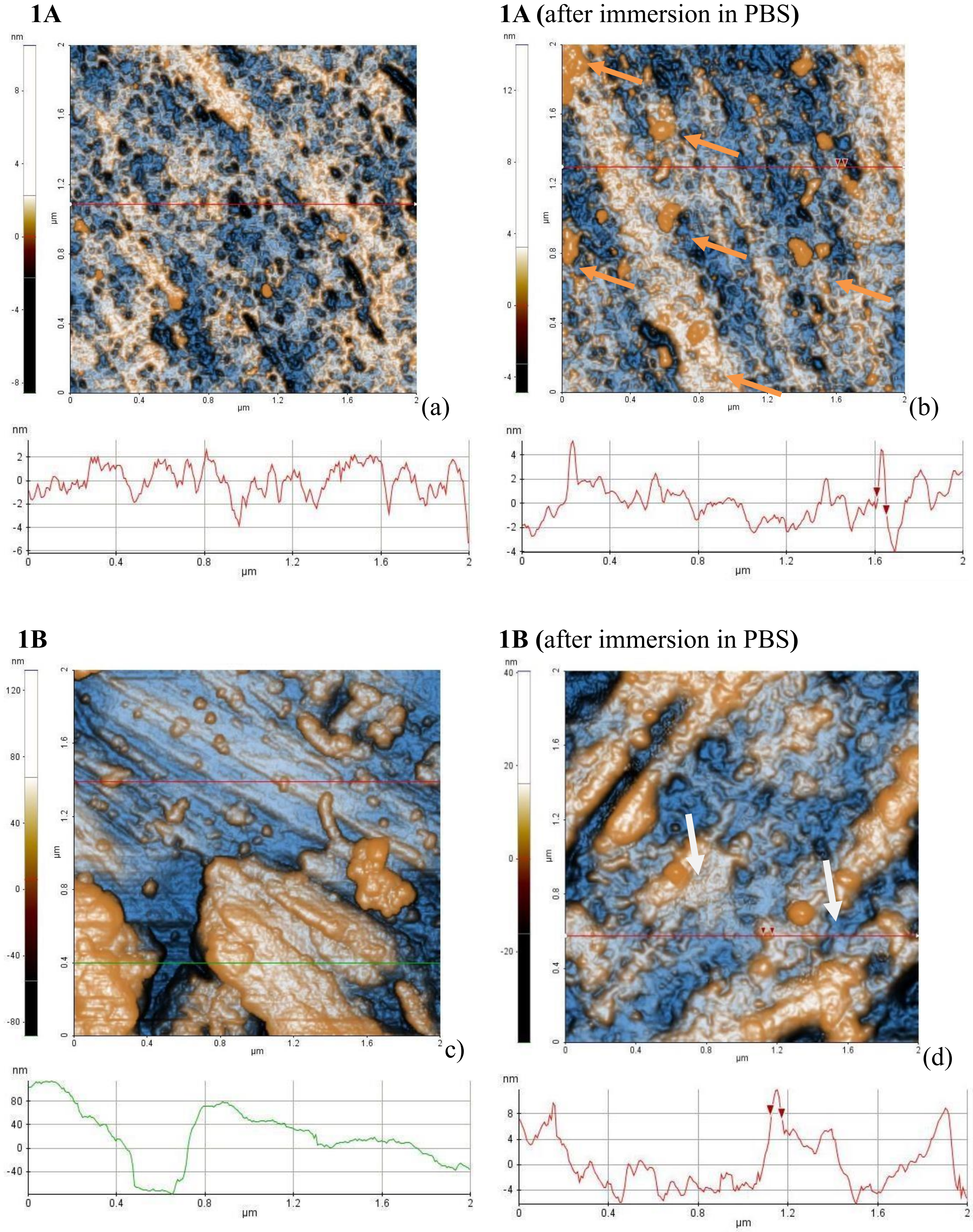


Fig. 5.1 Contrast-enhanced 2D AFM images (topography) recorded at the scale of (2µm x 2µm) for sample 1 (Ti20Ta9Nb8Zr2Ag): a- sample 1A- polished before immersion in PBS; b- sample 1A- polished after 1000 hours of immersion in PBS solution; c- sample 1B (rough sample before immersion in PBS; d- sample 1B- rough after 1000 hours of immersion in PBS solution;

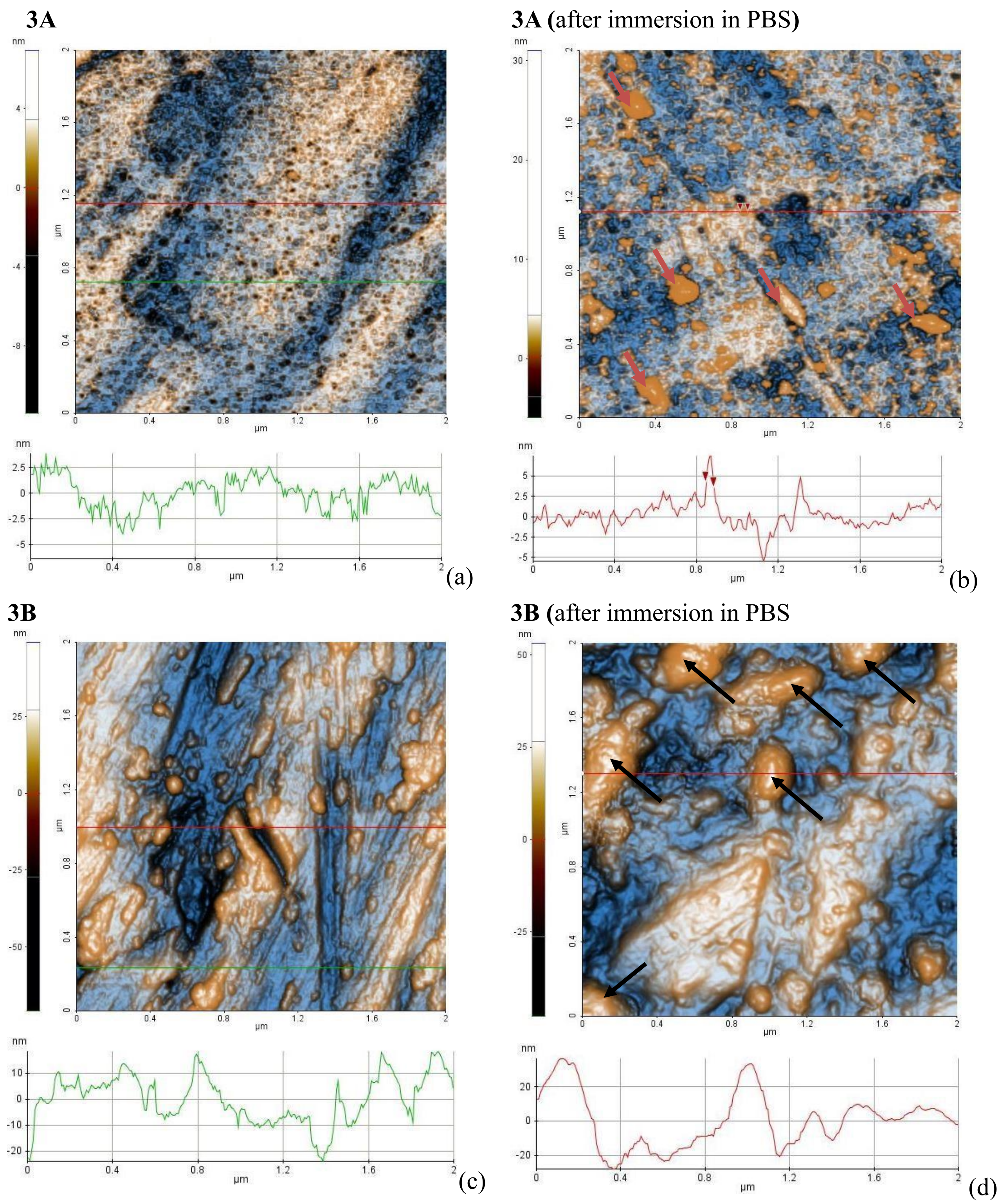


Fig. 5.2 Contrast-enhanced 2D AFM images (topography) recorded at the scale of (2µm x 2µm) for sample 3 (Ti10Ta9Nb8Zr2Ag): a- sample 3A- polished before immersion in PBS; b- sample 3A- polished after 1000 hours of immersion in PBS solution; c- sample 3B- rough sample before immersion in PBS; d- sample 3B- rough after 1000 hours of immersion in PBS solution;

5.1 Conclusions

Following research on the influence of the surface condition on the electrochemical behavior of alloys with different tantalum content in synthetic biofluids, the following partial conclusions can be drawn:

- The results highlight the influence of surface roughness on the formation of a passive layer that contains phosphate compounds and acts as a barrier layer against the corrosion processes that occur at the alloy/electrolyte interface.
- The Ta content does not influence, at least in the 10-20% range, the OCP value, the samples with 20%Ta and 10%Ta, respectively, have practically the same values after 1000 hours of immersion, but the surface roughness acts differently; thus, the polished samples (A), with low roughness are totally passivated after 100 hours, the OCP remains constant at approximately +70mV/Ag/AgCl, while the rougher samples (B) present an increased surface activity, the surface is more reactive and the OCP moves relatively continuously -with a very low speed of 125µV/hour- towards electropositive values. It should be emphasized that after 1000 hours of immersion in PBS at 37oC, the difference between the OCP of the two types of surfaces is below 100mV, i.e. both are passive.
- The Tafel analysis confirms the conclusion stated above, according to which the Ta content between 10% and 20% does not greatly influence the value of the corrosion rate, the samples with 1 and 3 have practically the same values after 1000 hours of immersion, but the surface roughness has a significant influence.
- It should be emphasized, however, that the alloy with 20% Ta in the polished state presents a lower stability of the surface, the anodic dissolution peak is wider, even if the current density values are in the range of 10-30µA/cm2.

Regarding the modification of the hydrophilic/hydrophobic character of the surface after contact with biofluids, the following conclusions can be drawn:

- The measurement of the contact angle in relation to water highlights the influence of the tantalum concentration on the hydrophilic nature of the alloy surfaces. Thus, the hydrophilic character is accentuated, at a concentration of 20%Ta the value of the contact angle decreases from 65° to approximately 35°.
- Based on the contact angle values using the OWKR method, the surface free energy and its components (polar and dispersive) were estimated.
- A tendency to increase the polar component of the free energy with increasing tantalum concentration was found, while the dispersive component shows an inverse variation. The surface free energy shows an increase with increasing tantalum concentration.
- The increase in surface energy indicates an increased reactivity of the metallic material, which favors, on the one hand, the interaction with the adjacent tissue, facilitating cellular adhesion, which can have the effect of osseointegration and mechanical anchoring of the implant.
- A methodology was developed based on the Cassie - Baxter model, for correlating the value of the experimental contact angle with the amount of phases present in the material. The weighted amount of alpha and beta phases estimated by this analysis was consistent with that estimated by SEM data analysis.
- Following immersion in artificial saliva, a significant change in surface energy is observed at a content of 15% Ta.
- As regards the modification of the hydrophilic character of the surfaces after immersion in

PBS, it is found that the contact angle decreases, so the hydrophilic character increases following the formation of the passivity film, which can have a positive influence on the osseointegration of the material.

Chapter 6. Experimental in vitro evaluation of the antimicrobial activity of the studied alloys

The toxicity testing of Ti-Nb-Ta-Zr type alloys with Ag was carried out using two research methods. The qualitative method of diffusion with alloy discs and the breaking point control method that attests the concentration at which the microorganism is inhibited (lack of growth) and the minimum inhibitory concentration (MIC) method were applied.

6.3 Conclusions

Alloys 0–5, in solid state, tested on the standardized microorganisms Escherichia coli ATCC 25922, Pseudomonas aeroginosa ATCC 27853, Staphilococcus aureus ATCC 25923 and Bacillus subtilis spp. had no toxic effect at the tested concentrations.

Lyzozym solutions, resulting from immersion in artificial saliva for 168 hours, showed a bactericidal and bacteriostatic effect on living cells, a fact that recommends them to be used in the medical field.

Chapter 7. Experimental research on the evaluation of the electrochemical behavior of the alloys developed in 3% NaCl solution

Electrochemical characterization was

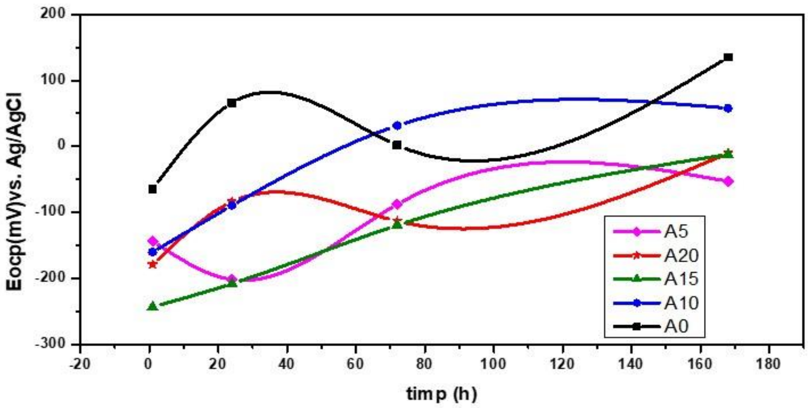
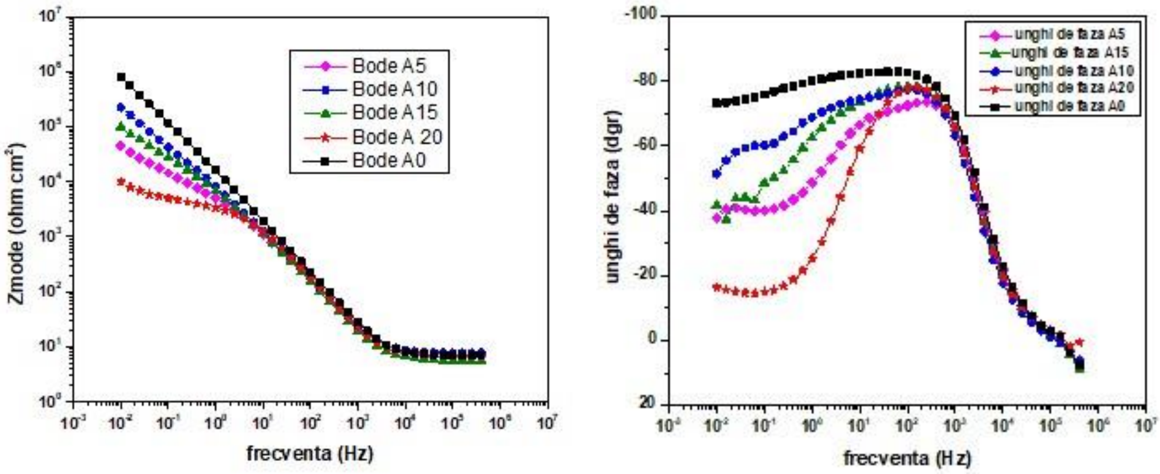


Fig. 7.1 Time evolution of the OCP of the experimental alloys immersed in 3% NaCl solution at a temperature of 37.5°C for 168 hours

7.2 Characterization of the behavior of alloys in 3% NaCl solution at 37°C by electrochemical impedance spectroscopy (EIS)

The electrochemical behavior of the alloys revealed from the Tafel curves, were also confirmed by the EIS tests whose response is presented in the form of Bode (figure 7.3) and Nyquist (figure 7.4) curves. Figure 7.3a corresponding to the Bode plots illustrates the decrease in polarization resistance with increasing tantalum content in the alloy, simultaneously with the increase in resistive behavior.



(a) (b)

Fig. 7.3 EIS representations obtained after 168 hours of immersion in 3% NaCl solution at 37.5°C on all samples: (a) Bode plots; (b) Bode plots -phase angle.

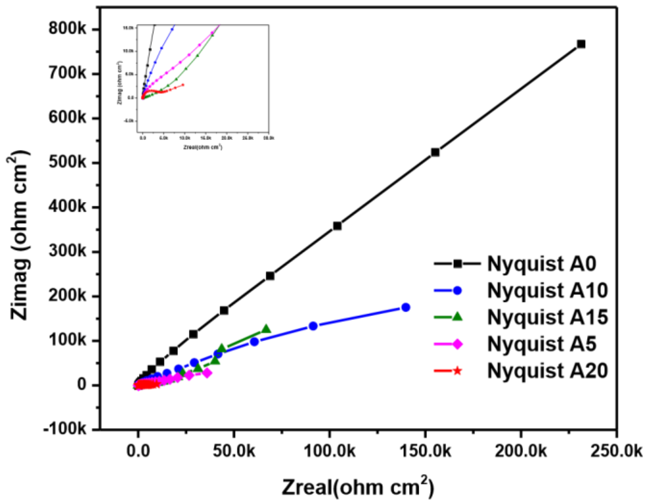


Fig. 7.4 EIS, Nyquist diagrams, obtained after 168 hours of immersion in 3% NaCl solution at 37.5°C on all samples; (in set: high frequency diagrams)

7.3 Experimental results regarding the determination of corrosion rates of alloys in 3% NaCl solution, by the Tafel slope method

Regarding the electrochemical parameters extracted from the Tafel curves (Figure 7.6), it is observed that after 168 hours of immersion in 3% NaCl solution, the equilibrium potentials of all alloys are much more electropositive than the corrosion potentials, which means that the alloys are spontaneously in a state of passivity.

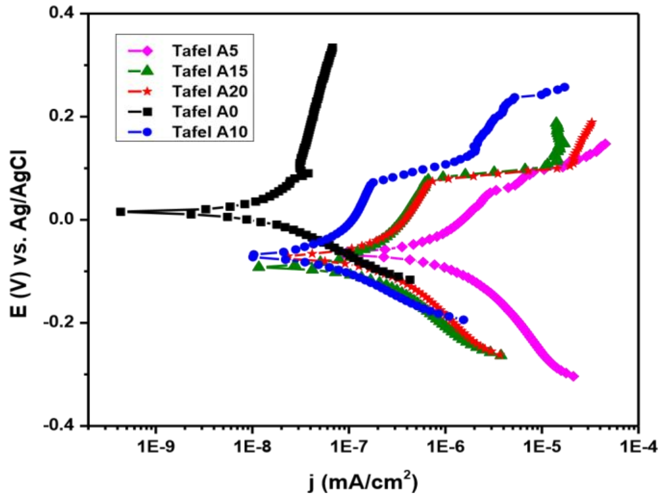


Fig. 7.6 Tafel curves of the alloys tested after 168 hours of exposure in 3% NaCl solution at a temperature of 37.5°C

7.4 Partial conclusions

- Tantalum shifts the stationary potential in a 3% NaCl solution at 37.5°C to more electronegative values by about 150-180 mV.
- Alloys with a Ta content between 10 and 20% show, in a 3% NaCl solution, more electropositive stationary potentials than corrosion potentials, which highlights the passivation tendency.
- Corrosion rates increase with increasing tantalum concentration in the alloy, but remain at relatively low values between 5 µm yr-1 and 47 µm yr-1.
- Ti10Ta9Zr8Nb2Ag alloy with 10% tantalum is shown to have the lowest corrosion rate

CHAPTER 8. Final conclusions, personal contributions and research directions

8.1 Final conclusions

The doctoral thesis "Development of new alloys with a low modulus of elasticity for biomedical applications" aims to design and develop a new alloy in the Ti-Nb-Zr-Ta-Ag system, their morphostructural and mechanical characterization and highlighting the parameters with major influence on its behavior in contact with synthetic biofluids: chemical composition, micro and macrostructure, surface condition.

The experimental research aimed at the design, simulation, optimization of a set of chemical compositions to meet the requirements, the elaboration of alloys and their morphostructural, mechanical and biocompatibility characterization. The results and discussions are structured in five chapters, and the conclusions will be presented in each chapter.

In the design chapter

1. An original methodology was developed which consists of a programmed experiment in several steps for the simulation/design of alloy compositions.

2. Formulation of the main requirements: modulus of elasticity as low as possible, lower than 80GPa and corrosion resistance in synthetic biofluids and antimicrobial activity.

3. A software was developed for calculating the electronic parameters (Bo and Md) from the Morinaga model using Wolfram Mathematica and Microsoft Excel applications.

4. Based on the calculated parameters, the mechanical characteristics of a large number of alloys from the TNZT system were estimated.

5. Mathematical modeling was carried out, the assessment of the weight of these parameters in relation to the estimated structure. The calculation matrix included the variation of the elements tantalum Ta = (0; 5; 10; 15; 20)% mass and niobium Nb = (9; 10; 11; 12)% mass.

6. Thus, an equation was established that describes a response surface for each of the three electronic parameters, and the accuracy of the proposed equations was verified.

7. The chemical composition of the alloy was optimized with the help of a specialized software (JmatPro).

8. One of the important conclusions of the theoretical simulation study was that tantalum has a more pronounced betagenic character than niobium, and changing its concentration generates a structure with a higher β-phase proportion at considerably lower concentration values than in the case of niobium.

In the elaboration and characterization chapter

1. Five alloys with real chemical compositions were developed.

2. Scanning electron microscopy studies have proven to be relevant for the appreciation, at an intimate level, of the morphology of the structural constituents, for the appreciation of the elemental distribution and the quantification of the chemical composition of the experimental alloys.

3. A working methodology was developed to evaluate the proportion of phases in alloys and the influence of alloying elements: micrographs obtained at magnifications of 5x103, 10x103, 20x103 and 40x103 were used, performing 12 random thickness measurements per magnification, thus obtaining 48 values/alloy. The values were processed statistically, and simultaneously the Anderson-Darling test, ANOVA analyzes were performed considering the tantalum concentration as an influencing factor and the lamella thickness as the response, using a significance level of 0.05. Simultaneously, a Tukey test was performed to compare the means.

4. The value of the modulus of elasticity decreases continuously with the increase of tantalum content in the alloy from 100GPa to 51GPa.

5. In the cast state these alloys show good mechanical characteristics, but their deformability requires remediation by heat treatments.

6. The tensile crack initiation of all alloys is type I.

7. In the case of the compression test, the microstructure has less influence on the mechanical characteristics than in the case of tensile stress, in the case of compression stress the crack initiation is type II.

8. When subjected to compressive stress, the cast alloy exhibits a stable, easily predictable mechanical behavior, the influence of the structure being much less.

9. With the increase in tantalum concentration, an increase in the coefficient of friction is observed, inverse variation in the case of lamella thickness: the greater the thickness of the lamella, the higher the coefficient of friction.

10. The scratch hardness shows an increasing trend with the increase in tantalum content, for alloy A0 its value is 3.6GPa, and at a content of 20%Ta a value of 6.09GPa is reached. *In the chapter evaluating the influence of the surface state on the electrochemical behavior of experimental alloys in synthetic biological environments*

1. The results highlight the influence of surface roughness on the formation of a passive layer that contains phosphate compounds and acts as a barrier layer against the corrosion processes that occur at the alloy/electrolyte interface.

2. The Ta content does not influence, at least in the 10-20% range, the OCP value, the samples with 20%Ta and 10%Ta, respectively, have practically the same values after 1000 hours of immersion, but the surface roughness acts differently; thus, the polished samples (A), with low roughness are totally passivated after 100 hours, the OCP remains constant at approximately +70mV/Ag/AgCl, while the rougher samples (B) present an increased surface activity, the surface is more reactive and the OCP moves relatively continuously - at a very low speed of 125µV/hour - towards electropositive values. It should be emphasized that after 1000 hours of immersion in PBS at 37oC, the difference between the OCP of the two types of surfaces is below 100mV, i.e. both are passive.

3. The Tafel analysis confirms the conclusion stated above, according to which the Ta content between 10% and 20% does not greatly influence the value of the corrosion rate, samples with 1 and 3 have practically the same values after 1000 hours of immersion, but the surface roughness has a significant influence .

4. It should be emphasized, however, that the alloy with 20% Ta in the polished state presents a lower stability of the surface, the anodic dissolution peak is wider, even if the current density values are in the range of 10-30µA/cm2.

5. Regarding the modification of the hydrophilic/hydrophobic character of the surface after contact with biofluids, the following conclusions can be drawn:

- the measurement of the contact angle in relation to water highlights the influence of the tantalum concentration on the hydrophilic nature of the alloy surfaces. Thus, the hydrophilic character is accentuated, at a concentration of 20%Ta the value of the contact angle decreases from 65° to approximately 35°.
- based on the contact angle values using the OWKR method, the surface free energy and its components (polar and dispersive) were estimated.
- a tendency to increase the polar component of the free energy with increasing tantalum concentration was found, while the dispersive component shows an inverse variation. The surface free energy shows an increase with increasing tantalum concentration.
- the increase in surface energy indicates an increased reactivity of the metallic material, which favors, on the one hand, the interaction with the adjacent tissue, facilitating cell adhesion, which can have the effect of osseointegration and mechanical anchoring of the implant. - a methodology was developed based on the Cassie - Baxter model, for correlating the value of the experimental contact angle with the amount of phases present in the material. The weighted amount of alpha and beta phases estimated by this analysis was consistent with that estimated by SEM data analysis.
- after immersion in artificial saliva, a significant change in surface energy is observed at a content of 15% Ta.
- regarding the modification of the hydrophilic character of the surfaces after immersion in PBS, the decrease of the contact angle is observed, therefore the increase of the hydrophilic character following the formation of the passivity film, which can have a positive influence on the osseointegration of the material.

The determination of the antimicrobial activity of the alloys was achieved through two approaches: the direct contact of the samples with culture media and the use of biofluids after immersing the samples for at least 168 hours.

1. Alloys 0–5, in solid state, tested on the standardized microorganisms Escherichia coli ATCC 25922, Pseudomonas aeroginosa ATCC 27853, Staphilococcus aureus ATCC 25923 and Bacillus subtilis spp. had no toxic effect at the tested concentrations.

2. Lyzozym solutions, resulting from immersion in artificial saliva for 168 hours, showed a bactericidal and bacteriostatic effect on living cells, a fact that recommends them to be used in the medical field.

Regarding the evaluation of the electrochemical behavior of the alloys developed in 3% NaCl solution

1. Tantalum shifts the stationary potential in a 3% NaCl solution at 37.5°C to more electronegative values by about 150-180 mV.

2. Alloys with a Ta content between 10 and 20% show, in a 3% NaCl solution, more electropositive stationary potentials than corrosion potentials, which highlights the passivation tendency.

3. Corrosion rates increase with increasing tantalum concentration in the alloy, but remain at relatively low values between 5 µm yr-1 and 47 µm yr-1.

4. Ti10Ta9Zr8Nb2Ag alloy with 10% tantalum is found to have the lowest corrosion rate.

8.2 Personal contributions

1. Writing a literature synthesis regarding the development of the Ti-Nb-Zr-Ta compositional matrix, as well as the methods that can be applied to improve their characteristics.

2. Development of an original methodology for the simulation/design of composites alloys;

3. Elaboration of the complex experimental program to fulfill the objective of the thesis; **4.** Development of a working methodology for evaluating the proportion of phases in alloys using micrographs at high magnifications, thus obtaining 48 values/alloy, which were processed statistically, through the Anderson-Darling test, ANOVA analyzes considering tantalum concentration as an influencing factor and in response the lamella thickness, using a significance level of 0.05. Simultaneously, a Tukey test was performed to compare the means.

8.3 Research directions

The experimental research carried out within this doctoral thesis and the results obtained, contributed to the establishment of new research directions:

- Improving the mechanical characteristics of the alloys obtained through thermo-mechanical treatments.
- Evaluation of the influence of the cooling speed on the morpho-structural transformation.
- Studying the superelasticity effect of the new alloys.
- Study of the mechanical parameters of the new alloys subjected to severe plastic deformation.
- Study of biocompatibility and corrosion behavior for materials in various thermomechanical processing situations.

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