TITANIUM ALLOYS WITH HIGH MECHANICAL RESISTANCE AND LOW ELASTIC MODULUS

PHD THESIS SUMMARY

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INTRODUCTION

One of the most important applications for titanium alloys with a high mechanical resistance and low elastic modulus is in their use as biomaterials for the manufacturing of bone implants.

The increase in the number and life expectancy of the global population has led to the unprecedented development of the use of implantable medical devices, devices that contribute to improving the quality of life of people affected by various diseases or traumas. For the fastest possible healing of various ailments, it is good that, from a wide range of high-performance implants, that devices suitable for each requirement can be chosen, which fulfil as faithfully as possible the functions of the organs / tissues they replace. However, these requirements are in a continuous dynamic, imposing an increase in implant performance, which depends, to a large extent, on the improvement of the properties of the biomaterials used to obtain these devices.

Among biomaterials, the metallic ones represent 70–80% of what is needed for the manufacture of implantable medical devices, and of these, titanium alloys are currently considered to be the most suitable for such applications. This is due to their excellent biocompatibility, high corrosion resistance, high mechanical strength, low density, and low elastic modulus. Titanium alloys do not show any form of toxicity or allergic reactions when in contact with the human body, but they show a strong tendency for osseointegration, this last characteristic being an important advantage for permanent implants with a bone interface.

In the human body, implant materials can be subjected to corrosion, high mechanical loads (through multiaxial loading, fatigue stress), but also to friction, which leads to the release of wear products in the body that can damage adjacent tissues.

In order to meet the requirements of the clinical applications for which they are intended, implants - and therefore the metallic biomaterials from which they are manufactured - must fulfil a set of biological, mechanical, and chemical properties. Some of these can be obtained by designing suitable compositions for Ti alloys, using for alloying chemical elements with high biocompatibility (Nb, Zr, Ta) and performing the synthesis of these materials with high-performance equipment, under appropriate working conditions and at optimal parameters.

The mechanical properties of titanium alloys (tear resistance, ductility, toughness, resistance to fatigue and crack propagation) and their corrosion behaviour strongly depend on their microstructure; these properties improve as the microstructure becomes finer. An important method for improving the microstructure of alloys is thermo-mechanical processing, which represents the set of plastic and thermal modelling operations applied to the initial material to obtain a material with improved properties. Depending on the initial constituent phases (alpha + beta, beta) and the processing schemes (the set of deformation processes and heat treatments, including the values of the processing parameters and the working environment) that were applied, the microstructure of a titanium alloy shows important changes at the end of its processing. These structural changes occur as a result of some transformation phenomena / mechanisms that take place in different stages of the alloy processing, at certain values of the processing parameters.

In this context, *the research in this doctoral thesis is aimed at developing knowledge related to how plastic deformation and heat treatments applied to some titanium alloys intended for bone implants contribute to improving their properties*.

The doctoral thesis is developed according to the requirements of the Regulation on the organization and conduct of DOCTORAL University Studies in the Materials Science and Engineering Doctoral School of the POLITEHNICA University of Bucharest, in article format.

CHAPTER I. PRESENTATION OF THE DOCTORAL THEME, CONCEPTS AND METHODS

I.1 TITANIUM ALLOYS USED IN THE MANUFACTURE OF MEDICAL IMPLANTS. PHENOMENA AND TRANSFORMATIONS SPECIFIC TO TITANIUM ALLOYS. THE OBTAINING AND THERMAL AND MECHANICAL PROCESSING OF TITANIUM ALLOYS

I.1.1 METAL ALLOYS USED AS BIOMATERIALS

I.1.1.1 General considerations on biomaterials

Research regarding medical devices leads to their diversification, specialization, and improvements in their functionality, as the properties of the biomaterials used to make these devices are refined. The rapid growth of scientific knowledge in the field of medical devices has raised the level of required properties for biomaterials. Currently, the development of biomaterials aims at a deeper understanding of the relationships between material and tissue, in order to obtain materials that imitate biological systems (biomimetic), and requires a broad knowledge of the properties of materials for the entire life cycle, as well as the interactions of medical products with biological systems [5].

The requirements for biomaterials can be divided into three categories, which are presented in order of their importance: clinical, manufacturing, economic. To develop an acceptable final product, factors such as toxicology, mechanical requirements, manufacturability, biocompatibility, ethical requirements must be considered. Among these factors, the greatest impact on the safety and efficacy of biomaterials are their biocompatibility and toxicity.

From the point of view of the component materials, biomaterials can be divided into three main categories: i) synthetic (metals, polymers, ceramics, composites); ii) derived from nature (e.g. plant-derived, tissue-derived); iii) semi-synthetic or hybrid biomaterials [7].

I.1.1.2. Metallic biomaterials

a) General considerations regarding metallic biomaterials

Degenerative and inflammatory bone and joint problems affect millions of people. Chronic diseases of the bone system are found in people over the age of 50 and require, in many cases, surgical interventions to replace the degraded natural joints. In addition to these, bone fractures, osteoporosis, scoliosis, and numerous other musculoskeletal diseases must be cured by using permanent, temporary, or biodegradable implants. Metallic biomaterials are systems that are designed to provide internal support to biological tissues - by replacing or repairing bone tissue - and are mostly used in joint replacements, dental implants, orthopaedic fixations, and stents [11, 4]. Metallic materials represent the most important class of biomaterials, representing approximately 70-80% of all materials used for the manufacture of implants. In Figure no. I.1.3, several metallic materials used in the manufacture of implantable medical devices are presented.

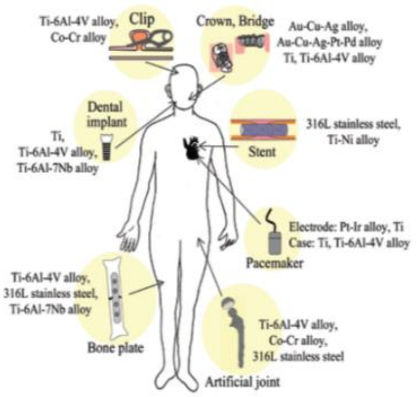

Fig. no. I.1.3–*Medical devices and metallic biomaterials used in their manufacture [13]*

b) Characteristics / properties required for metallic biomaterials

Many of the metallic biomaterials are used for the manufacture of implants that are necessary to heal various defects caused by degenerative and inflammatory diseases of bones and joints, bone fractures, congenital defects (scoliosis) and many other musculoskeletal diseases. Implants (sutures, bone plates, joint replacements, spinal fixation devices, etc.) and medical devices (pacemakers, artificial hearts, blood tubes, etc.) are used to replace and / or restore the function of traumatized or degenerated tissues or of organs, thus improving the quality of life of patients. However, implantation represents a potential assault on the chemical, physiological and mechanical structure of the human body.

A biomaterial used in the manufacture of implants must possess some important properties that allow its long-term use inside the body without the occurring of the phenomenon of rejection.

Figure no. I.1.4 schematically presents the requirements for orthopaedic implants.

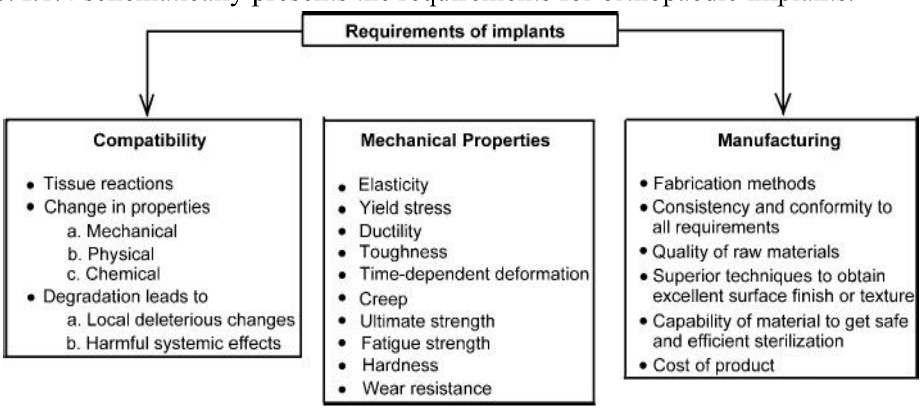

Figure no. I.1.4 - *Requirements for orthopaedic implants*

Until recently, the research work carried out in the field of metallic biomaterials was mainly focused on *biochemical compatibility*, with a first main requirement related to obtaining superior corrosion resistance [14]. Currently, an additional requirement for implants relates to the *mechanical biocompatibility* of the materials from which these devices are manufactured, with it being as important as the biochemical compatibility [14, 15], mainly when considering implants designed for a long life. Mechanical biocompatibility aims to match the mechanical properties of biomaterials with those of living tissue and is expressed by an appropriate level of Young's modulus, as well as by fracture resistance, ductility, fatigue life, wear resistance properties, functionality, etc. Maximizing these properties is a great challenge in the case of crystalline materials, as their fracture toughness and elastic modulus tend to increase or decrease simultaneously [14]. The Young's modulus of metallic materials is generally much higher than that of the human cortical bone, and this causes bone atrophy due to the stress shielding effect between the implant and the bone [16]. Therefore, the Young's modulus of metallic biomaterials must be as close as possible to that of bones.

c) Metallic materials used as biomaterials

In general, metals have been used for the manufacture of load-bearing implants such as hip and knee prostheses and for fracture fixation (pins, screws, and plates) [3]. Unlike pure metals (Au, Ta, etc.), that are occasionally used in various applications, alloys give medical devices, especially implants, the mechanical properties necessary to ensure a long life-cycle. Three groups of materials dominate biomedical metals: stainless steel, cobalt-chromium-molybdenum alloys, and titanium and titanium alloys. There is also a group of materials used for the manufacture of biodegradable implants (Mg and Zn alloys).

Table no. I.1.1 – *Mechanical properties of metallic biomaterials compared to cortical bone [17]*

Material	Young's modulus, E (GPa)	Yield strength, s_y (MPa)	Ultimate strength, s_{UTS} (MPa)	Elongation (%)
Stainless steel	200 - 205	170 - 690	540 - 1000	12 - 40
Co-Cr alloys	220 - 230	450 - 1500	655–1.900	5 - 30
Titanium (Ti)	100 - 115	170 - 480	240 - 550	15 - 24
Cortical bone	10 - 20	-	100 - 300	1 - 2

Stainless steel is the generic name for several different steels, that are used - mainly due to their resistance to a wide range of corrosive agents, easy availability, low cost, excellent manufacturing properties, acceptable biocompatibility and high strength - for a wide range of applications which help in fracture healing, in joint components and in vascular stents. The most used material in this group is austenitic stainless steel [18].

Co-Cr alloys are used especially for making artificial joints due to their high wear and corrosion resistance and acceptable biocompatibility. As a result of growing concerns about the release of Co (and Cr) ions, alternatives based on ceramic components (Al_2O_3, Al_2O_3-ZrO_2) are growing in popularity and tending to replace these materials [3]. CoCrMo alloys [Cr (27 - 30 %), Mo (5 – 7 %), Ni (2.5 %)] are used in dentistry and to make artificial joints, and CoNiCrMo alloys [Cr (19 – 21 %), Ni (33 – 37 %) and Mo (9 – 11 %)] are used in the manufacture of hip or knee joint prostheses.

Titanium and its alloys have seen the fastest growth in the metal biomaterials market, being considered the most suitable biomaterials for implantation due to their excellent biocompatibility, high mechanical and corrosion resistance, low density, and relatively low elastic modulus. Titanium and its alloys are used for the manufacture of orthopaedic implants and are used almost exclusively for endosseous dental implants, an application that requires implants with good fatigue resistance characteristics. The advantage of Ti-based alloys is mainly due to the high resistance to corrosion in vivo, due to the stable passive oxide (TiO2) layer that is rapidly formed on the surface of the implant. Titanium and its alloys show a strong tendency to osseointegration, this characteristic being another important advantage for permanent implants with a bone interface. The elastic moduli of Ti alloys have much lower values (and, implicitly, closer to the values of human bone) compared to other metallic biomaterials. Figure no. I.1.5 presents the elastic moduli for various commercial and experimental titanium alloys and the elastic moduli for Co-Cr alloys, 316L stainless.

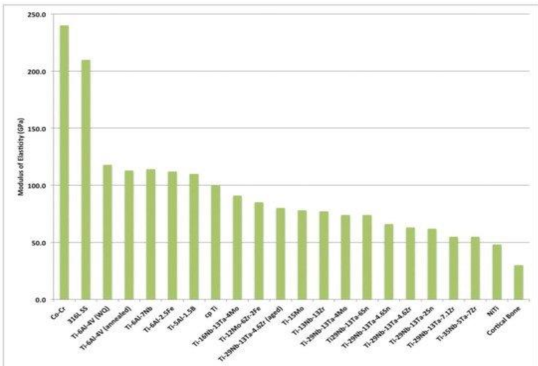

Fig. I.1.5 – Elastic modulus E (GPa) for different materials [21]

I.1.2 TITANIUM AND TITANIUM ALLOYS

I.1.2.1 Titanium

Titanium has a wide range of physical properties, mainly due to allotropy, when in its solid state. The crystalline structure of titanium is given by the temperature and pressure to which it is subjected and can be classified into three phases: i) Ti α, the low temperature phase, with a hexagonal compact structure (hcp), which is stable below 882 °C; ii) Ti β, the high temperature phase with a centred cubic (bcc) structure, which is stable from 882 °C to 1667 °C and iii) Ti ω - the high pressure phase, which has a hexagonal structure. Figure no. I.1.6 shows the hcp and bcc type structures that can be taken by titanium.

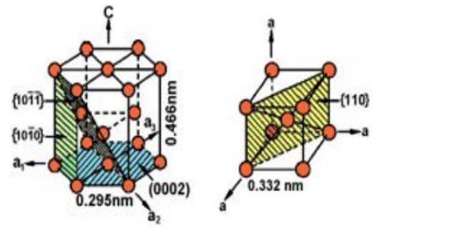

Figure no. I.1.6 – *Crystalline structure of titanium: a) Ti α – hexagonal compact structure; b) Ti β- cubic structure [35]*

In pure titanium, the transition from the α phase to the β phase is by allotropic transformation and occurs when the α phase is heated to a temperature called the β-transus temperature (882 °C). The transition between α and β phases is influenced by the purity of titanium. The addition of some elements to Ti alloys has a strong effect on the transformation temperature. If the elements increase the transformation temperature (stabilize the α phase), then they are called α-stabilizers - Al, O, Ga, Y, N, Ge, C. Similarly, if the elements lower the transformation temperature (stabilize the β phase), then they are called β-stabilizers. Depending on the effect they have on the β phase, the β-stabilizing elements are divided into elements that lead to a completely stabilized β phase (β-isomorphic elements) - Mo, Nb, Ta, W, V - and elements that lead to a partially stabilized β phase (β-eutectoid elements) - Cr, Mn, Fe, Si, H, Co. Some titanium alloys also contain "neutral" alloying elements (Zr, Sn, Hf), which have an insignificant impact on β-transus temperatures. Fig. I.1.7 shows the effect of alloying elements on the β-transus temperature.

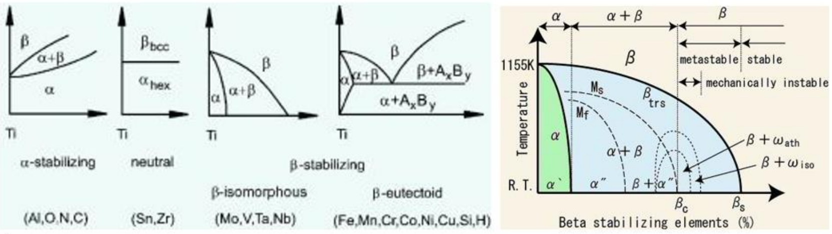

Figure no. I.1.7 – *The effect of alloying elements on the β-transus temperature [35]*

Due to its characteristics, titanium is widely used in several industries (aeronautics, biomedical, chemical, nuclear, architecture, etc.).

I.1.2.2 Titanium alloys

Ti alloys can be classified, depending on their majority phases, into three main categories: α alloys; α + β; and β. It is possible for α-type alloys to contain a small amount of β-phase and, conversely, for β-alloys to have varying amounts of α-phase. For this reason, two subcategories were introduced: near-α alloys (which have a small amount of the β phase) and β -metastable alloys (which have a small amount of the α phase).

α-type titanium alloys can have large amounts of substitutional alloying elements, including Al and Sn, as well as interstitial alloying elements such as O, C, and N dissolved in the hcp crystal structure, and small amounts of elements which do not dissolve in the crystal matrix, such as Fe, V and Mo. The practical limit of the amount of α-phase stabilizing elements that can be added to titanium is about 9 %, after which, due to an ordering reaction, the alloys tend to embrittle. Examples of common α alloys are Ti-5Al-2.5V (used in cryogenic applications) and Ti-6Al-2Sn-4Zr-2Mo (from which turbine components are manufactured). A major disadvantage of α-titanium alloys is the difficulty of modelling them by cold plastic deformation [33]. Near-α alloys have been developed to be processable by forging for the manufacture of components that operate in higher temperature, high wear environments, such as aircraft gas turbine engine compressors. Near-α alloys contain up to 2 % β stabilizing elements.

α + β titanium alloys contain a combination of α and β-stabilizing elements and present a grain structure composed of α and β phases, having three different types of microstructures - fully lamellar, bimodal, and fully equiaxial microstructures -, and each type of the microstructure provides different mechanical properties. The composition of α + β alloys and their thermal and mechanical processing determine the distribution and relative volumes of the two phases (α and β respectively). Because they present properties characteristic of both the α phase and the β phase (high hardness, good fatigue behaviour and corrosion resistance) this type of alloys are used in a wide range of applications (aeronautical, automotive, chemical, medical, etc.). The most commonly used alloy is Ti-6Al-4V, used in pressure vessels, turbine blades and medical implants. Another alloy widely used in various industries is the Ti-6Al-7Nb alloy. More recently, new vanadium-free α+β alloys have been developed: Ti5Al1.5Fe1.4Cr1.2Mo; Ti15Mo2.8Nb3Al; Ti15Sn4Nb2Ta0.2Pd0.2O; Ti20Nb; Ti5Al3Mo4Zr [34].

β-titanium alloys are very highly alloyed alloys, with large amounts of β-stabilizing elements such as molybdenum, niobium or tantalum. β-phase alloys can be subdivided into near-β alloys, β-metastable alloys, and stable β alloys. A fourth category is β-matrix (or β-rich) α + β Ti alloys, which can be included in the broad classification of β-phase alloys, although they can also be classified as α + β double-phase Ti alloys. The β-metastable phase alloys consist mainly of the β bcc phase but, depending on the composition and thermal and mechanical processing, may also contain small volume fractions of martensitic phases or the athermal ω phase. In general, β-metastable Ti alloys are designed and heat-treated to retain nearly 100 % of the bcc β-phase volume when cooled from the single-phase β domain to room temperature. This is achieved by alloying with sufficient amounts of β-phase stabilizing elements to suppress the formation during cooling of the hcp α′ martensitic phase, the α″ orthorhombic martensitic phase and the hcp α equilibrium phase.

Compared to α-type alloys, β-alloys are easier to deform, including when cold (due to the volume-centred cubic structure), and show better diffusion of elements during processing. In addition, among titanium alloys, β-type alloys have the highest hardness and fracture toughness.

Due to their unique combination of properties (high mechanical strength, excellent heat treatability, a high degree of hardening, outstanding hot and cold workability, properties that can be substantially improved by mechanical processing and heat treatments [35]), such as age hardening, β-type titanium alloys are very attractive for several applications in various fields. β-metastable / stable titanium alloys can have a low elastic modulus, close to that of human bones, and a high degree of resistance in biological fluids, being particularly suitable for biomedical applications. A new generation of β -Ti alloys with low elastic modulus (in the range of 70 - 90 GPa), which do not contain Ni, V and Al, have been made with β-stabilizing and biocompatible elements such as Nb, Ta, Zr and Mo (Ti13Nb13Zr super β-type alloys and Ti15Mo β-type). Two β-type alloys—Ti13Nb13Zr and Ti12Mo6Zr2Fe (TMZF)—were developed in the early 1990s and were used to manufacture hip prostheses. In the last decade, alloys such as Ti29Nb13Ta4.6Zr and Ti35Nb7Zr5Ta have received increasing attention due to their low elastic modulus (65 and 55 GPa, respectively).

I.1.3 PARTICULARITIES OF PHENOMENA AND TRANSFORMATIONS OCCURING IN TITANIUM ALLOYS

I.1.3.1 Cold plastic deformation phenomena/mechanisms in metastable titanium β alloys

Metallic materials that are subjected to external stresses first deform elastically (when the deformation disappears with the disappearance of the external stresses), then plastically (when the applied forces exceed the elastic limit and the deformation persists after the disappearance of the external stresses) and finally break, when the stresses pass of certain critical values.

The mechanisms of cold plastic deformation of single crystals (at temperatures below the recrystallization threshold) are: slip deformation, deformation by twinning and deformation by a mixed mechanism.

Slip, which represents the main mechanism of plastic deformation, with it being the mechanism of large deformations, consists of the movement of packages of atoms along crystallographic planes.

Twinning is the secondary mechanism of plastic deformation, with it being the mechanism of small deformations, and is characteristic of materials with few slip planes. Twinning consists in the collective and coordinated displacement of the atoms of a crystal area along some crystallographic planes (twinning planes) resulting in two or more parts with crystal lattices symmetrical with respect to the twinning plane.

The plastic deformation of monocrystals by a mixed mechanism starts by slipping, until the slipping planes are exhausted, and continues by twinning, when a part of the crystallographic planes rotates, becoming favourable to slipping. When an intense slip occurs, the crystallographic planes tend to rotate to become parallel or perpendicular to the direction of stress, which leads to the arrest of slip deformation. These rotations are compensated in some areas in the crystal, called secondary slip bands, by so-called Taylor rotations. Therefore, the plastic deformation of a crystal is produced by a complex mechanism, which involves both slips, as the predominant mechanism, as well as twinning and Taylor rotations [43].

The deformation of polycrystalline materials - which are made up of a large number of crystals with different orientations of the sliding planes in the network - occurs according to the same mechanism as in the case of monocrystalline ones, but with more difficulty and not simultaneously in all crystals, because it is conditioned by the boundaries between the crystal grains (which make deformation by sliding more difficult) and by the processes that take place in the neighbouring crystals.

Plastic deformation of metals is mainly achieved by shearing, when lattice planes in the material slide over each other, allowing the macroscopic shape to change without majorly affecting the ordering and arrangement of the atoms within the structure. The plastic deformation of metals depends on the generation and subsequent movement of dislocations and begins when the stress on the dislocations reaches a critical level [44].

Shear stress can also be obtained by a *twin-induced plasticity* (TWIP) mechanism, which is a very different mechanism from dislocation movement. Since it can occur in materials subjected to both compressive and tensile stresses, along the stress axis, in order to better measure the performance of the alloy, it is necessary to anticipate the successful activation of the predominant twinning system. Twinning in titanium alloys is achieved by mechanical deformation or by annealing following plastic deformation.

Ti β alloys can undergo structural transformations both by dislocation slips and by the mechanism of twin-induced plasticity. The content of stabilizing β elements can influence the dominant deformation mechanism; thus, in stable β alloys, the dominant mechanism is dislocation slip, and in metastable β alloys the dominant mechanism is TWIP [48, 49].

I.1.3.2 Phase transformations phenomena / mechanisms in metastable titanium β alloys

The properties of titanium alloys are primarily determined by the morphology, volume fractions and specific properties of the contained phases. Therefore, the change by phase transformation of the volume fractions in a titanium alloy leads to a change of its properties.

A phase transformation in a metallic material occurs when one or more of its phases change their crystal structure. Phase transformations in the solid state can be divided into: i) diffusion transformations, which require the movement of atoms from the initial lattice to the final location by diffuse, random jumps over distances of the order of atomic distances (or larger); ii) displacement transformations (which include martensitic transformations), where the movement of atoms can be achieved by homogeneous distortion, mixing of lattice planes, static displacement waves or a combination thereof [50].

The martensitic transformation is characterized phenomenologically by assigning several temperatures. The most common of these are: Ms, the temperature at which martensite begins to form during quenching; Mf, the temperature at which the transformation is complete. At the Ms temperature, the initiation of the martensitic reaction depends on the shear modulus of the alloy at the transformation temperature, the magnitude of the homogeneous shear associated with the transformation, and the magnitude of the inhomogeneous shear. *The chemical driving force required for the martensitic reaction at the Ms temperature can be supplemented by applying an external stress and/or plastic strain, leading to the formation of stress-assisted, stress-induced, or strain-induced martensite* (TRIP) [50].

The strength and ductility of titanium β alloys are dependent on their microstructure. The fracture resistance of these alloys can be improved by reducing the grain size and by precipitating in the β-phase grains a small amount of the α″ phase, which would constitute a barrier to slip propagation. However, the amount of transformed α″ phase must be controlled and limited in order not to affect the ductility of titanium alloys.

Elementary mechanisms such as TRIP and TWIP in metastable β-alloys have been investigated mostly through the lens of their chemical composition and their approaches to hardening (precipitation mechanisms). However, the physical mechanisms that lead to obtaining the mechanical properties in these alloys are not fully elucidated, which justifies the need for further research to clarify these aspects.

I.1.4 SYNTHESIS OF TITANIUM ALLOYS

I.1.4.1 Synthesis methods for titanium alloys

a) *The synthesis of titanium alloys in melting furnaces* is the simplest method of synthesising titanium alloys which, by completely melting the constituent elements, ensures the homogeneity of the composition of the ingots. The resulting alloy can be cast directly into the desired shape (close to the finished shape), or into ingots which can then be thermally and mechanically processed, depending on needs. The major disadvantage of this method is given by the high production costs and the costs of purchasing the synthesis equipment, which must be able to raise the working temperature to values that ensure the melting of all the component elements and ensure a high vacuum or an inert atmosphere for preventing the high hot gas reactivity of titanium and some of its alloying elements.

b) *Obtaining titanium alloys through powder metallurgy*. *Powder metallurgy* (PM) is a cheap, simple, and versatile synthesis method, with sintering temperatures much lower than the melting points of the constituent elements. Through PM, parts with shapes and sizes very close to the final ones can be obtained, thus reducing their processing costs. An advantage of PM methods is the many options for producing porous samples (currently, porosities from 5% to 37% can be obtained), achievable by careful control of powder morphology and of the degree of compaction. However, due to poor inter-particle interconnectivity, sintered metal parts with high porosities tend to exhibit poor mechanical properties, lack strength, are brittle, and prone to fatigue crack propagation even at low stresses [52].

Additive manufacturing (AM) is a method currently used in a wide range of fields. In the medical fields, additive manufacturing aims to meet the personalized (individual) anatomical needs of patients and to develop tissue and organ engineering by printing cells and complex architectures (scaffolds) from multiple materials to achieve tissue regeneration. In order to obtain a model containing the anatomical surfaces of the patient, AM uses computer-aided design and modelling (to process the data of 3D images of the anatomical structure obtained from the patient using a computer tomograph). The model is then used to generate data for rapid implant prototyping with high dimensional accuracy and complex tissue- and organ-like structures.

c) *Forming methods by spraying*. Spray forming involves obtaining the desired shape by successive spray deposition of a powder or molten mist (resulting from volatilization of a target).

I.1.4.2 Synthesis of titanium alloys by furnace melting

a) The influence of alloying elements in the synthesis process by melting Ti alloys

Specific weight. The alloying elements of alloys generally have specific weights that are much different from that of Ti, the parent metal. From the point of view of the process of obtaining the alloy, the differences between the specific weights of the constituent elements require a very good agitation of the batch during the elaboration process, in order to obtain a homogeneous chemical composition throughout its mass and to avoid the formation of segregations.

Melting point and boiling point. The melting and vaporization temperatures of the elements in the composition of an alloy can show significant differences. In the elaboration process, it is necessary that the temperature in the melting furnace can ensure the melting of all the elements, but the boiling temperature of any element must also not be exceeded. Otherwise, corrections to the calculation of the material quantities must be taken into account for the preparation of the batch.

Reciprocal reactivity of metals. Binary phase diagrams show that the metals in the composition of the alloys are often mutually reactive. In order to obtain a stable and homogeneous structure for the alloy, it is necessary to melt the charge in a controlled regime of temperature increase, in order to incorporate all the metals in the melt so that no un-melted metal inclusions remain. Furthermore, in order to achieve a fine-grained structure, it is necessary, in addition to homogenization with intensive mixing, for a rapid cooling such as to avoid grain growth.

Reactivity to gases. When heated, titanium and its alloys interact with gases in the atmosphere, resulting in superficially deposited or dissolved chemical combinations, with the obtained effect being that of hardening of the metallic material. The oxidation speed intensifies simultaneously with the increase in temperature, and after the appearance of the oxide film, a layer rich in dissolved gas is also formed.

Considering the above, when synthesizing Ti alloys, it is necessary to take into account the following aspects that will have a major influence on the quality of the obtained alloy: i) the elaboration of the alloy in a closed environment, in a vacuum or controlled inert atmosphere; ii) the strong reactivity of the main elements in the composition of the alloy towards gases - oxygen, nitrogen, hydrogen - required the avoidance of gas impurification of the metal both during the elaboration process and during subsequent processing; iii) the use of metals of the highest possible purity, the control and maintenance of impurity elements within precisely established limits. All this imposes that *the method of producing titanium alloys is melting in a high vacuum (10-*

^{3} – 10^{-4} torr) or in a controlled inert atmosphere, in an aggregate that ensures the complete melting of the metals, the homogeneity of the alloy and a low level of impurities, especially gaseous ones.

b) The influence of the melting process on titanium-based alloys

When determining the appropriate melting process for the elaboration of a titanium alloy, the following aspects are taken into account, which impose certain requirements for the elaboration process: i) alloys usually contain elements with a wide range of melting temperatures, which influences the choice of the synthesis process , that must ensure the melting of all the elements in the composition of the alloy; ii) controlling and gradually increasing the temperature until all constituent elements melt; iii) very good homogenization of the molten bath; iv) rapid cooling of the cast metal.

The main manufacturing processes of titanium-based alloys, each of them presenting advantages and disadvantages, are: melting in an electron beam furnace; vacuum arc melting and consumable electrode furnace; melting in a graphite resistance furnace; induction melting in a cold crucible furnace.

• *Magnetic levitation cold crucible melting* (CCLM) is a clean melting method, without contamination of the molten material, which can be used for melting metals with very different melting points and of reactive metals. The process allows for the obtaining, at a very high speed, of homogeneous alloys, thanks to a strong effect of stirring of the melt, which can be cast directly into the desired shape. Melting and casting of the material can be done in a vacuum or inert gas atmosphere. The temperature that can be reached in the cold crucible furnace depends on the physical characteristics of the material: electrical resistivity; viscosity; specific weight; homogeneity. The working pressure has a limit of $3x10^{-8}$ mbar.

I.1.5 PROCESSING OF TITANIUM ALLOYS

I.1.5.1 General considerations on metal processing

The mechanical properties of alloys (tear resistance, ductility, toughness, resistance to fatigue and crack propagation) and their corrosion behaviour strongly depend on their microstructure.

An important method for improving the microstructure of alloys and, implicitly, their properties is thermal and mechanical processing, which represents the set of plastic and thermal modelling operations applied to the initial material to obtain a material with improved properties. *This processing does not have the same effect for all titanium alloys; for this reason, in order to obtain a final product with appropriate mechanical properties, it is necessary to adapt the heat treatment and mechanical deformation scheme for each individual alloy, knowing well the relationship between the microstructure and its properties.*

In *mechanical processing*, the most important characteristic is the material's *deformability* which consists of its ability to sustain advanced plastic deformation without suffering integrity problems and is the result of the combination of its plasticity and deformation resistance properties.

A good plasticity of alloys can be obtained by complying with the following requirements: i) the synthesis of metallic materials with a suitable chemical composition (without elements that reduce their plasticity), with a uniform structure in terms of grain size and shape, with chemical homogeneity and with a relatively uniform distribution of impurities in their volume (plastic properties can be improved by a homogenization heat treatment); ii) processing under optimal conditions of temperature and deformation rate (if the plasticity at room temperature is high enough, the plastic deformation of the alloys must be done by cold working, otherwise, the plastic deformation is carried out hot; the decision regarding the cold or hot processing of the alloys, must take into account other factors such as the structure, type and number of constituent phases, etc.); iii) the use of an appropriate atmosphere in the heat treatment aggregates (the heat treatment must be carried out in an atmosphere that avoids gas impurification of the metal); iv using processing methods that maximize deformation uniformity; v) processing in a state of tension to increase the plasticity indices as much as possible.

Depending on the application considered for the metal material and the phase structure of the alloy, heat treatments may be performed after plastic deformation to improve the final mechanical and structural properties of the alloy. The *heat treatment* is the basic metallurgical process by which the optimization of hardness, fracture toughness and fatigue strength of alloys can be achieved.

The size, volume fraction, morphology and spatial distribution of α-precipitates formed during thermal and mechanical processing of titanium alloys have an essential influence on the mechanical properties of the final product. Grain size is considered a central microstructural parameter for controlling the physical, chemical, mechanical, and biochemical properties of polycrystalline materials. Therefore, to obtain the desired functional properties, grain size control is one of the most important factors to be considered. To achieve enhanced material performance, techniques have been introduced to fabricate ultra-fine grained (UFG) structures through severe plastic deformation (SPD) techniques [57]. SPD is a metal deformation process generally used to achieve very large plastic deformations in a metal to create ultra-fine grain sizes. The strength of materials increases in value as the grain size becomes finer. The ultra-fine grain also allows super-plastic deformation of the alloys at moderate temperatures and high strain rates. The motivation behind using an SPD process is to produce lightweight, high-strength parts.

I.1.5.2 "Classical" mechanical processing methods of titanium alloys

Processing by plastic deformation of metal bodies involves changing their shape and dimensions (without affecting their integrity), having the effect of changing their structure and, implicitly, their properties. There are several classical plastic deformation processes of titanium alloys, the most important being: rolling, forging, extrusion, drawing.

a) *Forging* is the process of plastic deformation of a material through the action of compression forces (static, for presses, or dynamic, for hammers) between two surfaces of the processing equipment. Forging can be simple (when flat tools are used) or in a die (when tools are used that have cavities of the same configuration as the desired part). In the case of forging and moulding titanium and its alloys, it is necessary to apply high unit strain rates, but with low total reduction rates, so that the recrystallization process can be kept under control. *The upper limit* of the optimum temperature range for forging will rise by 20...100 °C, depending on the type of alloy. For all types of alloys, the lower limit of the hot deformation temperature must not be below 700 °C. In most cases, this temperature varies between 800 and 850 °C [58].

The temperature ranges for the main titanium alloys for both β forging and α+β forging are presented in Table no. I.1.6.

Table no. I.1.6 - *Forging start and end temperatures*

Alloy	Beta forging		Alfa + beta forging	
	Forging starting T, °C	Forging end T, °C	Forging starting T, °C	Forging end T, °C
Grade 1-4 commercially pure Ti	980	815	815	760
Ti5Al2,5Sn	1150	955	1065	950
Ti8Al1Mo1V	1175	1010	1040	920
Ti8Mn	980	815	900	705
Ti6Al4V	1150	925	955	850
Ti7Al4Mo	1175	955	1010	860

The purpose of β-forging is to reduce the cross-section of the blanks, but also to destroy the coarse casting structure of the ingots and transform it into a new, much finer, (deformation) structure, with improved properties. The α+β forging is the one at the end of which the mechanical properties and microstructure required for the blanks must be obtained. The resulting mechanical properties after forging can be improved by an appropriate heat treatment, through which the structure obtained during forging will transform into a new structure, which must ensure the isotropy of the mechanical properties, as well as the targeted values for these properties.

b) *Rolling* is the most common plastic deformation process, in which a material is passed between two rotating parts. The material is driven by friction into the space between the cylinders, which is called the deformation zone or focus. Lamination can be longitudinal, when the parts are cylinders rotating in opposite directions, or transverse / transverse-helical, where the parts are truncated, bitronconical or disc-shaped and rotate in the same direction. Through rolling, the size of the material is reduced in the direction of the force, and its dimensions are increased in the other two directions. Thus, rolling is mainly used to obtain long pieces with a constant section, but also to obtain complicated finished products. The pieces obtained by this process have a structure with fine crystals, with superior mechanical properties to cast ones.

c) *Extrusion* is the process in which, using a compressive force, the material is passed through the opening of a mould, the deformation taking place inside the crystals, by sliding and twinning. It can provide a blank area reduction of up to 90% or even more in a single operation.

d) Drawing are processes that consist of passing the material that is to be processed through the calibrated drawhole of a mould (in the case of draw) or wire die (in the case of draw with back pull) by using a traction force. The material section is gradually reduced in the process.

I.1.5.3 Severe Plastic Deformation processes for titanium alloys

A granulation with ultra-fine / nanometric structure cannot be obtained by the usual plastic deformation processes, which is why new techniques of severe plastic deformation (Severe Plastic Deformation – SPD) have been developed. When using ordinary metal deformation processes, for example rolling, the plastic strain obtained is less than 2.0; if the material is rolled several times, the plastic strain can be greater than 2.0.

The use of SPD for the processing of titanium alloys with improved properties has seen a major development as the ability of these techniques to improve the ultra-fine / nano structure of the grains and their properties such as fracture resistance, induced deformation, hardness, wear, corrosion resistance and biocompatibility was proven. Products deformed by SPD have higher wettability and higher surface energy. The attachment and proliferation of fibroblast and osteoblast cells are enhanced on nanostructures due to their higher bioactivity that induces apatite precipitation and causes greater adsorption of adhesive proteins [62]. Therefore, one of the most suitable areas for the use of ultra-fine-grained materials is that of medical devices such as bone implants.

The nanostructuring of metallic materials increases the mechanical strength of the material, including fatigue resistance, due to the hardening and refinement of the microstructure, while also having a positive effect on the corrosion behaviour. Having superior mechanical properties, a permanent implant made of nanostructured Ti alloy can be significantly smaller, with improved geometry and therefore be less harmful to the patient [64]. Furthermore, surface modifications of nanostructured nanomaterials provide the opportunity to develop and design implantable medical devices that perform better and offer improved functionality compared to their counterparts that are made of common coarse-grained materials [64]. Table I.1.8 shows the improved mechanical properties of commercially pure Ti (CP Ti) after nanostructuring. The mechanical strength of nanostructured titanium is almost double compared to CP Ti. The increase in strength was achieved under conditions where the total elongation to break is above the 10% limit.

Table no. I.1.8 – *Mechanical properties for coarse and nanostructured grade 4 Ti and, for comparison, the annealed Ti-6Al-4V ELI alloy [64]*

Nr.	Processing	UTS (MPa)	YS (MPa)	Elongation (%)	Fatigue resistance at 10^6 cycles
1	Grade 4 Ti with course structure	700	530	25	340
2	Nanostructured grade 4 Ti	1240	1200	12	620
3	Annealed Ti-6Al-4V	940	840	16	530

Several SPD techniques have been developed (about 120 methods, which shows the huge potential of this type of processing for industrialization), the most important being: i) High pressure torsion (HPT); ii) Equal channel angular pressing (ECAP); iii) Accumulative roll bonding (ARB). Other important SPD processing techniques are: i) Multi-pass Rolling (MPR); ii) Reciprocating extrusion-compression (REC); iii) Cyclic close die forging (CCDF); iv) Repetitive corrugation and straightening (RCS); v) Multi-axial Forging (MAF); vi) Twist Extrusion (TE); vii) Straightening and Repetitive Corrugation (SRC); viii) Asymmetric Rolling (AR).

I.1.6 HEAT TREATMENT PROCESSES APPLIED TO TITANIUM ALLOYS

By thermal treatment one refers to the set of technological operations of heating, maintaining and cooling at certain temperatures, with certain heating and cooling speeds, to which a material is subjected, the purpose of these operations being the modification of the technological and operational properties of the metal material by changing its structure.

The main stages of this type of process are: i) heating; ii) maintenance, when the temperature is equalized in the treated material and the structural transformation processes are completed; iii) cooling (Figure I.1.49 (a)).

The process parameters for the three stages of the heat treatment are: i) the final temperature and the rate at which the temperature increases to heat the material; ii) the temperature and duration of keeping the material at a constant temperature; iii) the initial temperature for the cooling stage and the duration of the cooling process.

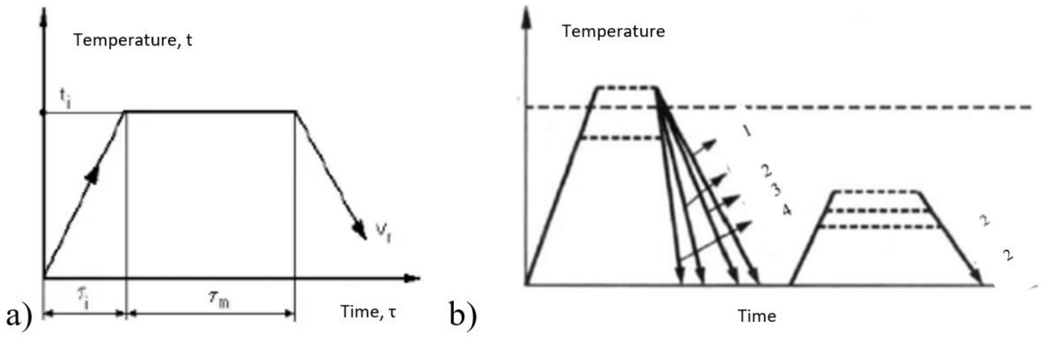

Figure no. I.1.49 – *Main diagram for a heat treatment: a) simple; b) in two stages (1 – cooling in the oven; 2 – air cooling; 3 – oil cooling; 4 – water cooling)*

According to the pursued purpose, and the place it occupies in the manufacturing process, heat treatments can be: i) preliminary, when applied to ingots, cast or forged parts, welded parts, etc. to correct some of their defects or to prepare them for further processing and consists of different types of annealing; ii) finishing, which is applied to the material after it has been mechanically processed and consists mainly of quenching and tempering.

Heat treatment of titanium alloys can lead to simultaneous high strength and good plasticity. Titanium alloys are heat treated to obtain: i) an optimal combination of ductility, machinability, dimensional stability, and structural stability; ii) reduction of residual stresses developed during processing; iii) improvement of special properties. Combinations of different heat treatment processes are used to optimize material properties (fracture resistance, fatigue resistance, creep resistance at high temperatures, resistance to preferential chemical attack), preparing alloys for plastic deformation (forging, rolling, etc.) or for further forming and processing operations.

The β-transus temperature plays an essential role in heat treatments, as it is the parameter with which phase transformations can be determined. The response of titanium alloys to heat treatment depends on both their composition and the effect of heat treatment on the alpha-beta phase balance. *Due to differences in composition and microstructure, but also because the alloys are intended to be used in various applications that require specific property sets, not all heat treatments are applicable to Ti alloys*.

Next, the main types of heat treatments applied to titanium alloys are presented.

a) A **de-stressing treatment** is applied to samples containing residual stresses due to non-uniform cooling or plastic deformation (after non-uniform hot forging or cold working, after asymmetric machining of plates or forgings and after welding and cooling of castings) and performed by slowly heating the samples to a temperature below the β-transus transformation zone, maintaining this temperature followed by slow cooling, usually in the oven in which they were heated. The holding time must be long enough to ensure stress relief without producing an undesired amount of precipitates, aging for α+β or β alloys, or undesired recrystallization of single-phase alloys. Residual stresses decrease progressively as a function of temperature and holding time. Stress relief performed on titanium alloys does not adversely affect their mechanical strength or ductility.

b) **Annealing** consists of heating the metallic material to a high temperature followed by holding it at this temperature long enough and slowly cooling it to produce a refined microstructure. For titanium alloys, common annealing treatments are: i) incomplete annealing; ii) duplex annealing; iii) recrystallization annealing; iv) beta annealing [82].

Incomplete annealing is a general-purpose treatment applicable to all rolled products. The value of the annealing temperature influences the size of the grains and their orientation. Annealing improves the fracture toughness, yield strength and total elongation of Ti alloys.

Duplex annealing changes the shape, dimensions, and phase distributions of alloys for which improved creep resistance or ultimate strength is required. In duplex annealing, the first annealing can be near the β-transus temperature to globuliza the deformed α phase and minimize its volume fraction. After cooling in air, the structure is not stable enough, so a second annealing at a lower temperature is required to precipitate the new α lenticular (acicular) phase between the globular α particles. The formation of the acicular α phase is associated with improvements in creep and fracture strength. The microstructure of the annealed alloy is more uniform and closer to equilibrium [86]. Duplex annealing treatment is used to achieve maximum creep strength and stability in near-α alloys (such as Ti8Al1Mo1V and Ti6Al2Sn4Zr2Mo) as well.

Recrystallization annealing and *β annealing* are used to improve the ultimate strength of titanium alloys. In *recrystallization annealing*, the alloy is heated to the upper limit of the α-β range, held for a time, and then cooled very slowly. In general, recrystallization annealing without phase transformation is applied to cold plastically deformed metal products, with the aim of restoring the plasticity of the materials by partially or totally eliminating the quenching state. Phase transformation annealing (at high temperature) is a heat treatment usually used on forged pieces that have a chemical composition different from the standard one, in order to achieve maximum toughness. Alloys processed by deformation in the α+β range are annealed in two stages. For the Ti-6Al-4V alloy, the first step is 1h at 945 ºC, followed by furnace cooling to 760 ºC, holding on the stand for 2h and then cooling in air. In this type of treatment, the crystallization process occurs by nucleation and growth of crystals resulting in the end in a material with a new structure, with the atoms returned to their equilibrium positions, with a low density of dislocations, without internal stresses and with high plastic properties, which allow the plastic deformation processes to continue. During the recrystallization process, depending on the holding time, a homogenization of the chemical composition can also occur, which improves the plasticity of the material [42].

Like recrystallization annealing, *β annealing* improves fracture toughness. β-annealing is done at a temperature slightly higher (to prevent excessive grain growth) than the β-transus temperature of the treated alloy. The holding time for annealing depends on the thickness of the sample section and should be long enough so that a complete phase transformation is achieved, but at a (minimum) level to control β-phase grain growth.

The best plasticity and thermal stability can be obtained by *isothermal annealing*, which is suitable for two-phase titanium alloys with a high content of stabilizing β elements. Isothermal annealing involves a step-by-step cooling, meaning that after heating above the recrystallization temperature, the alloy is immediately transferred to another furnace with a lower temperature (generally 600 ~ 650 ℃), then air-cooled to room temperature.

In α-β titanium alloys, thermal stability is a function of β phase transformations. During cooling from the annealing temperature, the β phase can transform and under certain conditions form a brittle intermediate phase known as the ω phase. A *stabilization annealing* treatment ensures that a stable β phase is obtained, that is able to withstand further transformations when exposed to high temperatures while in operation. α-β alloys that are weak in β, (Ti-6Al-4V), can be air-cooled from the annealing temperature without affecting their stability.

c) Solution treatment and aging. The solution heat treatment is applied to alloys whose alloying elements can combine with each other to form intermetallic compounds. This treatment ensures a uniform distribution of the alloying elements in the alloy structure, obtaining an unstable state at room temperature, a state that is called a "solid solution". The process consists in heating the alloy to a specific temperature (if this temperature is lower than the minimum imposed value, the resulting mechanical properties will be below the required values; if the temperature is higher than the maximum imposed value, there is a risk of overheating, cracking or burning of the material, producing deterioration of mechanical properties), holding at this temperature for a certain time, followed by cooling at a controlled rate in oil, air or water. The unstable state can be preserved if it is followed by sufficiently rapid cooling (quenching) and if the alloy is kept at a low temperature. *Aging* is the thermal treatment of hardening of alloys (that were solution treated), which is characterized by obtaining in their composition a relatively uniform distribution of alloying elements (precipitation). Aging consists of reheating the alloy to a certain temperature for about two hours and cooling it in the furnace. The process ensures higher mechanical properties than those obtained by other methods.

d) Tempering and aging hardening. *Quenching and aging* is the main method of heat treatment and hardening of titanium alloys, with the used mechanism being phase transformation. Hardening depends on the properties, concentration, and heat treatment specifications of the alloying elements, since these factors affect the type, composition, amount, and distribution of metastable phases obtained by quenching, as well as the nature, structure, and degree of dispersion of precipitates in the process of metastable phase decomposition [86].

Quenching involves heating the alloy (above β-transus) so that the phase transformation is obtained, followed by a sudden cooling; it is usually used to obtain martensitic structures in the treated material. Depending on the type of alloy and the concentration in β-gene elements, certain martensitic structures are obtained by quenching: i) α´, which is a solid solution supersaturated with β-gene alloy elements, with a deformed hexagonal network, presenting a structure with a lamellar-acicular appearance and having a hardness that is greater the higher the concentration of β-gene elements; ii) α″, which is a rhombic lattice martensite and which has a lower hardness than α′; iii) βx, which is a β solid solution supersaturated with alloying elements and which, being unstable, partially transforms into the hexagonal lattice ω phase (coherently bound to βx) which embrittles the alloy; iv) at high concentrations of the alloying elements, upon rapid cooling, the β phase does not transform, becoming the supersaturated β phase (βs) or the stable, equilibrium β phase (βe) [89, 90]. Hardening has the disadvantage of thermal stresses between areas with different sections of the parts, as well as structural stresses.

I.2 PRESENTATION OF THE CONCEPTS AND RESEARCH METHODOLOGY USED IN THE PhD THESIS

I.2.1 PRESENTATION OF THE CONCEPTS USED IN THE PhD THESIS

The requirements imposed on metallic biomaterials intended for the manufacture of bone implants concern their properties: i) mechanical (tear resistance, plasticity, Young's modulus, fatigue resistance); ii) physical (density, magnetic properties); iii) chemical (resistance to various forms of corrosion, degradation through wear); iv) biological (biocompatibility, bioactivity).

Due to their excellent biocompatibility, high corrosion resistance, high mechanical strength, low density and relatively low elastic modulus, titanium and its alloys are considered to be the most suitable biomaterials for implantation. Moreover, titanium and some titanium alloys do not show any form of toxicity or allergic reactions when in contact with the human body, but show a strong tendency for osseointegration, this characteristic being an important advantage for permanent implants with a bone interface. Implants made of such materials will have a reduced risk of infection and a higher success rate, as well as a long period of use, which will eliminate the need for surgical reintervention. Thus, research on improving the properties of biomaterials is motivated by important societal, human and economic stakes, with the results of their implementation being able to increase the quality of life of patients.

Titanium alloys intended for the manufacture of bone implants must have biochemical compatibility (this refers to obtaining materials with superior corrosion resistance) ***and high mechanical biocompatibility*** (aimed at correlating the mechanical properties of biomaterials with those of living tissues and is quantified by the appropriate level of modulus Young, as well as by mechanical strength, ductility, lifespan when exposed to fatigue, wear resistance properties, etc.).

The mechanical properties of titanium alloys and their corrosion behaviour strongly depend on their microstructure. An important method for improving the microstructure of titanium alloys and, implicitly, their properties is their thermal and mechanical processing. In order to obtain a final product with appropriate properties, it is necessary to adapt a specific processing scheme for each individual alloy, starting from a thorough knowledge of the relationship between the microstructure and its properties.

In this context, ***the experimental research in this doctoral thesis is aimed at developing knowledge related to how the processing by plastic deformation and thermal treatments of some titanium alloys intended for bone implants contributes to the improvement of their properties.***

Among the titanium alloys, beta-type ones best meet the requirements of bone implant applications due to their unique combination of properties (high mechanical strength, low elastic modulus, high hardness, good corrosion resistance) that can be substantially improved by various plastic deformation processes and heat treatments.

Metastable beta titanium alloys can have a low elastic modulus, close to that of human bone, thus avoiding the occurrence of the "stress shielding" effect, and a high degree of resistance in biological fluids, ***being particularly suitable for biomedical applications***. The β-metastable Ti alloys consist mainly of the β bcc phase but, depending on the composition and thermal and mechanical processing, may also contain small volume fractions of martensitic phases or the athermal ω phase.

Considering the above***, two Ti alloys with original chemical compositions, non-toxic and non-allergic alloying elements, with a high potential in terms of obtaining of biomaterials with advanced properties. These alloys are:***

Ti-32.9Nb-4.2Zr-7.5Ta (mass %) (TNZT);
Ti-30Nb-12Zr-5Ta-2Sn-1.25Fe (mass %) (TNZTSF).

In the compositions of the two alloys, niobium, tantalum, and iron are β-stabilizing elements, and zirconium and tin are nearly neutral elements for β-phase stability. Currently, Nb, Ta and Zr are considered to be the safest, non-toxic, and non-allergic alloying elements in titanium alloys, with them being shown by research studies to have high cell viability, corrosion resistance, tissue compatibility and non-allergic properties. In addition to being an excellent β-phase stabilizing element, Fe contributes to grain refinement and increases the mechanical properties of Ti alloys, and at a content higher than 1% (mass %) suppresses the formation of orthorhombic α" and ω phases in these alloys. In addition, it is non-toxic, being an essential trace element for metabolic processes. Also, tin is neither a toxic element for the human body. In Ti alloys, the addition of Sn allows the control of phase transformations, helping to reduce the precipitation of the ω phase and, depending on the content, can increase the ductility and corrosion resistance of these alloys. Sn is a weak α stabilizing element.

The molybdenum equivalency (MoE) for the two alloys is as below.

MoE_{TNZT} = 0,28x32,9 (Nb) – 0,17x4,2 (Zr) + 0,22x7,5 (Ta) = 10,15

MoE_{TNZTSF} = 0,28x30 (Nb) - 0,17x12 (Zr) + 0,22x5 (Ta) - 0,33x2 (Sn) + 2.9x1,25 (Fe) = 10,42

The range of conventional limits for metastable β-type Ti alloys is between 10 and 20 MoE. It therefore follows that ***the two alloys (TNZT, respectively TNZTSF) are of a metastable β type***.

As shown above, the properties of β-type Ti alloys can be substantially improved by various plastic deformation processes and heat treatments. *Metastable β-type Ti alloys may eventually undergo structural transformations through complex mechanisms induced by the application of external stress and/or plastic deformation, leading to the formation of stress-assisted, stress-induced, or strain-induced martensite (TRIP) or through a mechanism of twin-induced plasticity (TWIP).*

The experimental research in this thesis focuses on finding answers to the following questions:

⁕ What is the evolution of the characteristics of the microstructures of TNZT, respectively TNZTSF alloys after applying thermal and mechanical processing treatments to them?

⁕ What are the phase transformations occurring in the two alloys during thermal and mechanical processing?

⁕ What is the dependence between the microstructure obtained by thermal treatments and mechanical deformations of the two alloys and their mechanical properties?

The way in which the experimental research in the PhD thesis was approached is schematically presented in Figure I.2.1.

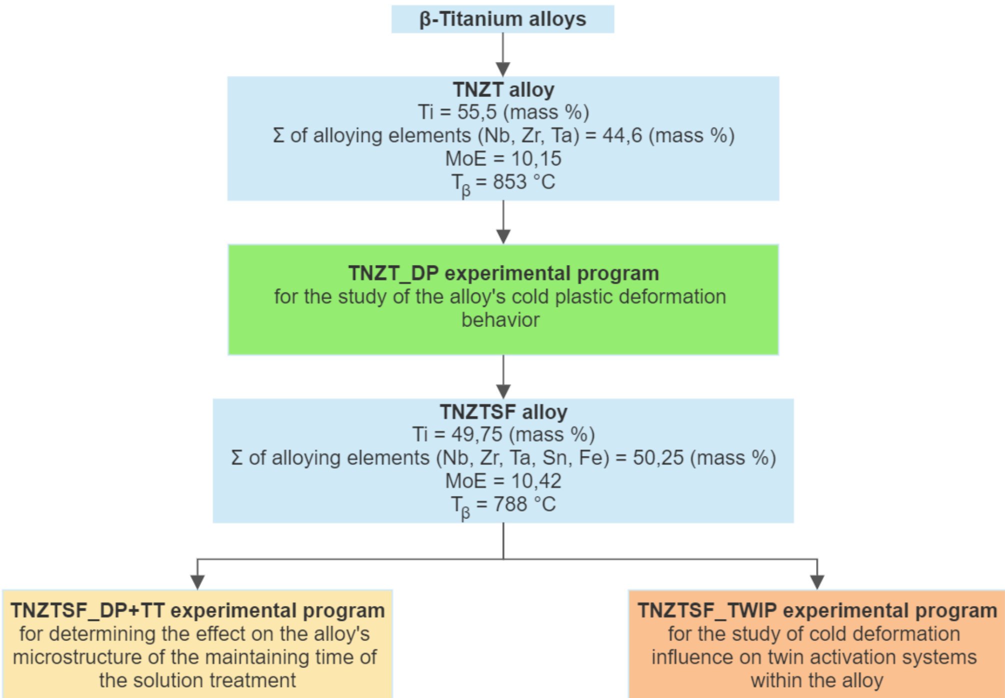

Figure no. I.2.1 – *Schematic representation of the approach to experimental research in the doctoral thesis*

This approach aimed, at a first stage, at establishing the influence of cold plastic deformation on the microstructure and properties of the alloy in the Ti-Nb-Zr-Ta system (which, in addition to Ti, contains alloying elements totalling 44.6% by mass), and then, after adding other elements (Sn, Fe), thus increasing the content of titanium alloying elements to 50.25 mass %, to evaluate the effect induced by a combined process of cold plastic deformations and heat treatments on the microstructure of the Ti-Nb-Zr-Ta-Sn-Fe alloy and to determine the evolution of the mechanical properties as a result of the structural changes that occurred. The targeted objective was to find an optimal combination of processing procedures and technological parameters that ensure the properties required for the use of alloys in the manufacture of bone implants.

I.2.2 OBJECTIVES OF SCIENTIFIC RESEARCH IN THE PhD THESIS

The main scientific objectives of the doctoral thesis were:

⁕ The development of knowledge related to how the microstructure of Ti-32.9Nb-4.2Zr-7.5Ta (mass %) and Ti-30Nb-12Zr-5Ta-2Sn-1,25Fe (mass %) alloys is modified by heat treatments and plastic deformation and the influence of these changes on their mechanical properties;

⁕ The study of the correlation between the conventional processing by cold plastic deformation and the microstructural and mechanical properties of the Ti-32,9Nb-4,2Zr-7,5Ta (TNZT) (% mass) biomaterial in order to obtain an optimal combination between the strength and ductility of the alloy for its intended applications in the biomedical field. To achieve this objective, the following stages were completed: i) synthesis of the alloy in a melting furnace with a cold crucible and its chemical characterization; ii) designing an appropriate route for alloy processing; iii) plastic deformation of the alloy by cold rolling with different degrees of deformation; iv) characterization of the cast and cold-rolled alloy from a microstructural point of view and of its mechanical properties;

⁕ Obtaining a microstructure and phase combination for the Ti-30Nb-12Zr-5Ta-2Sn-1,25Fe (TNZTSF) alloy (mass %) that would give it suitable mechanical properties for the manufacture of bone implants. Achieving this objective involved carrying out the activities included in the following stages: i) synthesis of the alloy in a melting furnace with a cold crucible and its chemical characterization; ii) designing an appropriate scheme for alloy processing; iii) plastic deformation of the alloy by cold rolling; iv) carrying out the thermal treatment by placing the rolled samples in solution; v) characterization of the alloy in its as-cast, cold rolled and after solution treatment states from a microstructural point of view and of its mechanical properties;

⁕ The study of the influence of the intensity of cold deformation on active twinning systems for the TNZTSF alloy. In order to carry out this study, these stages were completed: i) designing an appropriate program for alloy processing; ii) preliminary plastic deformation of the alloy by cold rolling; iii) treatment of laminated samples by solution treatment; iii) additional plastic deformation (with different degrees of deformation) by cold rolling of the samples previously subjected to solution treatment; iv) characterization of the microstructure of the alloy after the solution treatment, respectively after the additional laminations.

I.2.3 EXPERIMENTAL SCIENTIFIC RESEARCH STRATEGY

The experimental scientific research strategy in this PhD thesis focused on the establishment of processing schemes which, through the effect induced by the combination of plastic deformations and heat treatments on the microstructures of the two alloys, ultimately lead to obtaining appropriate mechanical properties (in particular a good ratio between strength and ductility properties) for the use of these biomaterials in implantology.

Next, the experimental programs established for the processing of the two alloys are presented.

Ti-32.9Nb-4.2Zr-7.5Ta alloy (TNZT)

a) The coded experimental program TNZT_DP aims to obtain, through cold plastic deformation, an optimal combination between the mechanical strength and ductility of the TNZT alloy that is intended for applications in the biomedical field. The plastic deformation scheme is presented in Figure I.2.2.

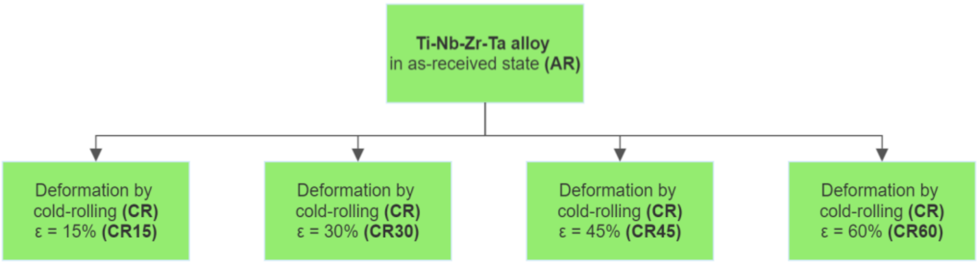

Figure no. I.2.2 - *Scheme for the coded experimental program TNZT_DP*

According to this scheme, the as-cast TNZT alloy (AR) is plastically deformed by cold rolling (CR) with different degrees of deformation: ε = 15 % (CR15); ε = 30% (CR30); ε = 45% (CR45); ε = 60% (CR60).

Plastic deformation induces changes in the microstructure and the mechanical properties of the TNZT alloy due to grain refinement and the variation of the ratio of the fractions of the constituent phases. These changes evolve with the increase in the degree of plastic deformation; when the degree of deformation increases, the mechanical properties (ultimate strength, yield strength as well as microhardness) increase, while the ductility decreases.

The as-cast and cold-rolled alloy with the 4 different degrees of deformation was characterized from the microstructural and mechanical properties points of view.

Ti-30Nb-12Zr-5Ta-2Sn-1.25Fe alloy (TNZTSF)

b) The coded experimental program TNZTSF_DP+TT aims to obtain a microstructure and combination of phases for the TNZTSF alloy, which will give it superior mechanical properties, that are necessary for the manufacture of bone implants, and is presented in Figure no. I.2.3. This program aimed to investigate how the mechanical and thermal processing conditions/parameters induce changes in the microstructure of the TNZTSF alloy, the aim being to obtain a microstructure with a homogeneous β-Ti phase, with equiaxed crystalline grains, with an average grain size of approx. 60 - 80 μm, with a low residual stress-strain field and a suitable combination of mechanical properties (high strength and ductility, low elastic modulus).

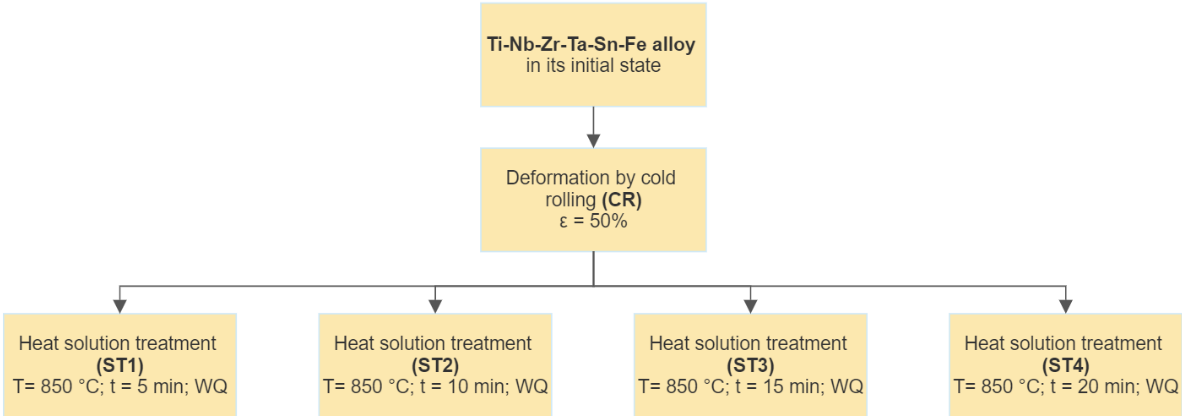

Figure no. I.2.3 – *Scheme for the coded experimental program TNZTSF_DP+TT*

The program consisted of cold rolling the as-cast TNZTSF alloy (I) to a total deformation degree of ε = 50% (CR), obtained in 5 equal steps, followed by solution heat treatment of four sets of samples , at the same temperature T of 850 ^{0}C but with different holding times t (5 min (ST1); 10 min (ST2); 15 min (ST3); 20 min (ST4)) - to establish the effect of the holding time on the microstructure of the alloy - and then cooling the samples in water.

The alloy in the as-cast, cold-rolled state and after the solution heat treatment was characterized from the point of view of microstructure and mechanical properties, in order to determine the influence that the treatment to which it was subjected had on its properties.

c) The experimental program coded TNZTSF_TWIP continued the investigations on the TNZTSF alloy by studying the influence of the intensity of cold plastic deformation on the activation of the twinning systems.

The chosen treatment scheme is the one shown in Figure I.2.4.

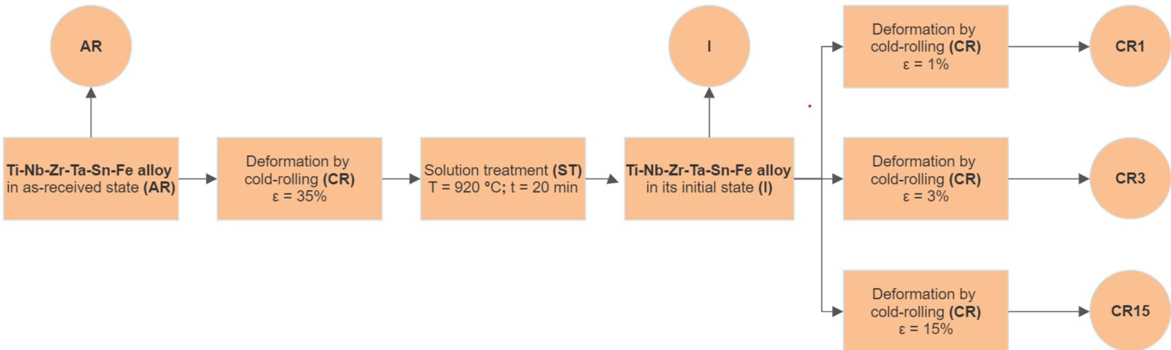

Figure no. I.2.4 - *Scheme for the coded experimental program TNZTSF_TWIP*

Through this experimental program, the as-cast (AR) TNZTSF alloy is preliminary plastically deformed by cold rolling, with a total deformation degree ε of approx. 35%, after which the rolled samples are thermally treated by solution treatment (ST) at a temperature T of 920 ^{0}C for 20 min. and then cooled in water. The alloy samples thus obtained (I) were additionally plastically deformed by cold rolling with different degrees of deformation: ε = 1 % (CR1); ε = 3% (CR3); ε = 15% (CR15).

Through the cold plastic deformation initially applied to the alloy, possible changes are induced in its microstructure, consisting of deformation bands, twinning systems, dislocation bands and an increased density of crystal network defects and residual stress-strain fields. An increase in mechanical strength and a decrease in ductility properties due to strain hardening are also possible.

The solution heat treatment applied to the alloy samples leads to the regeneration of the microstructure, which will present homogeneous equiaxial grains of β-Ti phase, with a size dependent on the duration of the treatment. The heat treatment also leads to the increase of the ductility properties of the alloy due to the decrease in the density of crystalline defects, the residual stress-strain fields and the increase in the average size of the grains. The additional deformation of the three samples aimed to establish the influence of the cold deformation intensity on the active twinning systems for the TNZTSF alloy.

The microstructure of the alloy after the solution heat treatment, respectively after the three additional cold rollings, was complexly characterized.

I.2.4 EXPERIMENTAL SCIENTIFIC RESEARCH METHODOLOGY

Alloy synthesis

When choosing the method and the alloy synthesis process, the properties of the alloying elements must be taken into account, which greatly influence the melting process. Following the analysis of the properties of the alloying elements of the two alloys (TNZT and TNZTSF) it was found that the following conditions must be respected during their synthesis: temperature control and gradual increase; melting in a closed, controlled atmosphere environment; avoiding gas contamination of the melt; good homogenization of the melt in the melting crucible; rapid cooling of the cast metal; the use of high purity alloying elements. All this required that:

- ***the method of producing the investigated Ti alloys should be melting in a controlled, inert atmosphere***, to ensure a low level of impurities, especially those of a gaseous nature;

- ***the process selected for the synthesis of the two Ti alloys is melting in a cold crucible furnace***, which presents a series of advantages such as: i) lack of contamination of the melted materials inside the crucible; ii) the high speed of the process; iii) metals with different melting points can be melted, including metals with extremely high melting points; iv) good homogeneity of the resulting alloys due to the strong electromagnetic agitation of the melt; v) the high cooling speed of the cast ingot allows for obtaining a fine grain structure; vi) vacuum or controlled atmosphere melting is possible.

The technological flow for the synthesis of Ti alloys in the cold crucible furnace consists of the following main operations: preparation of raw materials (Ti, Nb, Zr, Ta, Sn, Fe) by cutting; cleaning and removal of mechanical impurities in an ultrasonic bath; degreasing with volatile organic solvents; dosing of materials according to the batch calculation; loading the raw materials inside the crucible; achieving melting chamber vacuum; achieving the controlled atmosphere (Ar); melting the charge by adjusting the power of the electric generator; casting; cooling and evacuation of the ingot from the casting room; loading the ingot into the crucible for the second melting; the vacuuming of the melting chamber followed by the creation of the inert atmosphere (Ar); remelting the alloy; casting; cooling and evacuating the final ingot from the casting chamber and finishing it by cutting off the ends and turning. A Fives Celes MP25 cold crucible furnace (Fives Celes – France) was used for the synthesis of the alloys.

Considering the destination of the alloys, for medical applications, but also the restrictions imposed by obtaining the targeted properties, it is necessary to strictly observe the quality of the alloying elements used in the synthesis of these materials. The degree of purity of the raw materials influences the content of impurities in the final alloy, including gaseous ones (nitrogen, hydrogen) which are strictly limited. High purity elements were used for the synthesis of the studied alloys: Ti - min. 99.6 %, no. GF71176776; Nb - min. 99.9%, no. GF49338120; Zr - min. 99.5%, no. GF10742284; Your - min. 99.9%, no. GF80066392; Sn - min. 99.96%, no. GF11140928; Fe - min. 99.98%, no. 267945, from SIGMA ALDRICH/MERCH, Merck KGaA, Darmstadt, Germany.

Used sample sets

Samples from TNZT and TNZTSF alloys in the as-cast state (AR / I), without any processing, were used as a reference material in the comparative analyses with processed alloy samples, to highlight the evolution of their structural and mechanical properties.

In the coded experimental program TNZT_DP, 5 samples (AR) with a length of 40 mm, a width between 12 and 18 mm and a thickness of 0.80; 0.94; 1.14; 1.45 and 2.00 mm were cut from the cast TNZT alloy.

For the coded experimental program TNZTSF_DP+TT, 6 samples (I) with a length of 40 mm, a width between 12 and 18 mm and a thickness of 0.80 mm (1 sample), respectively 1.60 mm (5 samples – for cold rolling) were cut from the cast TNZTSF alloy ingots.

Similarly, ***for the coded experimental program TNZTSF_TWIP***, 4 samples (AR) with a length of 40 mm, a width between 12 and 18 mm and a thickness of 1.60 mm were cut from the TNZTSF alloy.

The cutting of samples from TNZT and TNZTSF ingots, respectively, was performed with a precision cutting machine MICRACUT® - 202 (Metkon Instruments - Turkey).

Alloy processing

The cold rolling of the two alloys, in all three experimental programs, was performed with an LQR120AS rolling mill (Mario di Maio – Italy). The reference system for sample deformation is presented in Fig. I.2.7.

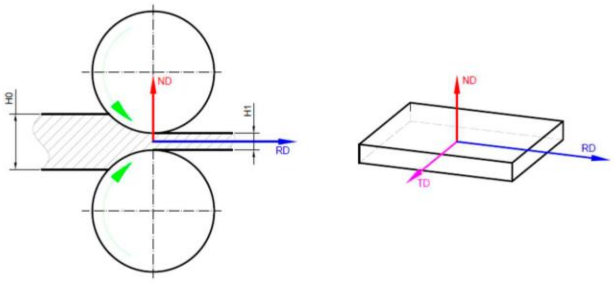

Figure no. I.2.7 – *The reference system for the deformation of samples by cold rolling (Rolling Direction - RD, Normal Direction - ND, Transverse Direction - TD)*

Through ***the coded experimental program TNZT_DP***, 4 samples of the TNZT alloy in the as-cast state (AR) with initial thicknesses of 0.94; 1.14; 1.45 and 2 mm were cold rolled with different degrees of total deformation of 15 %, 30 %, 45 % and 60 %, respectively (Figure I.2.8). The rolling speed was approximately 3 m/min (0.05 m/s).

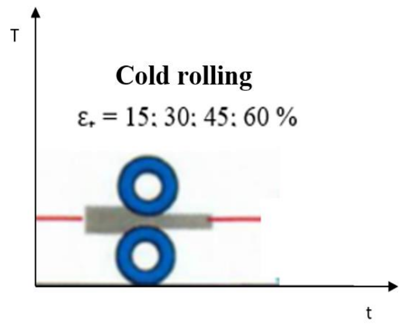

Figure no. I.2.8 - *Treatment scheme for the codified experimental program TNZT_DP*

Table no. I.2.1 presents the thickness values of the samples before and after their rolling.

Table no. I.2.1 - *Sample thickness values before and after secondary rolling from the experimental program TNZT_DP*

Initial state / Sample name	Sample thickness [mm]		Deformation degree, ε_t [%]
	Initial	Final	
As-cast / CR15	0,94	0.80	15
As-cast / CR30	1,14	0.80	30
As-cast / CR45	1,45	0.80	45
As-cast / CR60	2,00	0,80	60

Within the codified experimental program TNZTSF_DP+TT, whose scheme is presented in Figure no. I.2.9, the total deformation (AR) of the TNZTSF alloy samples, with the initial thickness of 1.6 mm was 50%, obtained in 5 equal steps of 0.16 mm/pass, the final thickness of the five resulting samples (CR) being 0.8 mm. The rolling speed was approximately 0.5 m/s.

The degree of total deformation is calculated according to relationship (I.2.1).

$$\varepsilon_t = \frac{h_\circ - h_f}{h_\circ} * 100\ [\%] \qquad (I.2.1)$$

where: ε_t – total degree of deformation [%]; h_0 - initial thickness of the sample [mm]; h_f - final thickness of the sample [mm]. In the present case, the values for h_0 and h_f were 1.6 mm and 0.8 mm, respectively.

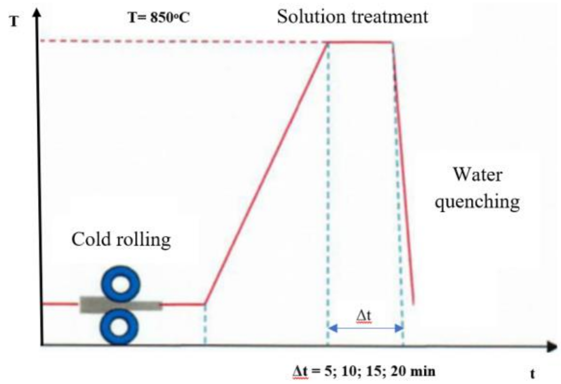

Figure no. I.2.9 - *Treatment scheme for the codified experimental program TNZTSF_DP+TT*

Four of the five cold-rolled samples with a total deformation degree of 50% were subjected to solution heat treatments, at the same temperature T = 850 0C, with different holding times t (5 min; 10 min; 15 min; 20 min), after which they were cooled in water. Considering the reactivity of titanium alloys towards gases at high temperatures, the heating of the samples was carried out under vacuum ($5x10^{-1}$ bar) in a GERO SR 100 X 500 furnace (Carbolite-Gero Inc., Germany). The heating speed of the furnace up to the temperature of 850 ^{0}C was 10 degrees/minute. Samples ST1, ST2, ST3 and ST4 were obtained as a result of this process.

In the coded experimental program TNZTSF_TWIP, a preliminary cold rolling of the 4 TNZTSF (AR) alloy samples with an initial thickness of 1.6 mm was performed, the resulting total deformation degree being approx. 35 %, obtained from three equal passes (approx. 0.2 mm/pass), and the final thickness of the samples (CR) after lamination being approx. 1 mm. The rolling speed was approximately 0.05 m/s.

The rolled samples with a total degree of deformation of 35% were subjected to a solution heat treatment at a temperature T of 920 ^{0}C, with a holding time of 20 min. and with water cooling (Figure I.2.10).

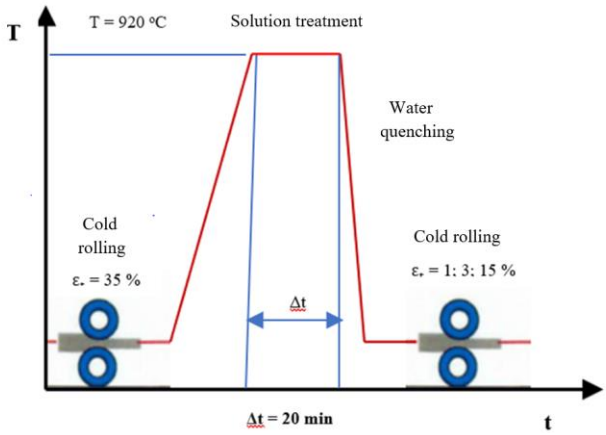

Figure no. I.2.10 - *Treatment scheme for the coded experimental program TNZTSF_TWIP*

The thermal treatment of solution treatment (ST) was carried out in a vacuum of $5x10^{-1}$ bars, in the GERO SR 100 X 500 furnace. The heating speed of the furnace up to the temperature of 920 0C was 10 degrees/minute.

After the solution heat treatment, three samples were cold-rolled with the LQR120AS rolling machine, with different degrees of deformation of 1% (CR1), 3% (CR3), and 15% (CR12), respectively, obtained by a single pass. The rolling speed was approximately 0.05 m/s.

Table no. I.2.2 shows the thickness values of the samples before and after the second rolling of the samples.

Tab. no. I.2.2 - *Sample thickness values before and after secondary rolling in the experimental program TNZTSF_TWIP*

Initial state / Sample name	Sample thickness [mm]		Deformation degree, ε_t [%]
	Initial	Final	
Solution treated / CR1	1,00	0,99	1
Solution treated / CR3	1,00	0.97	3
Solution treated / CR15	1,00	0,85	15

Characterization of the alloys studied in the doctoral thesis

Sample preparation for chemical and structural characterization. Samples necessary for the chemical and structural analyses were taken from the investigated alloys both in the as-cast state and in all stages of thermal and mechanical processing. Cutting the samples to the sizes required for their embedding was carried out with the MICRACUT® - 202 diamond disc cutting machine.

The samples were embedded in conductive phenolic resin (NX-MET XPHC) at 150 °C for 7 min using a BUEHLER SimpliMet hydraulic embedding press (BUEHLER - USA). The resulting sample holders had a diameter of 30 mm.

Using a DIGIPREP Accura machine (Metkon - Turkey), the embedded samples were ground in 5 steps (300 s/step) with SiC abrasive paper (NX-MET XPAC, Ø250, with grit ranging from 180 to 1200) and polished using a soft NX-MET M200 Ø250 mm felt and 6 and 1 μm NX-MET XP15 polycrystalline diamond slurry (300 s/step). Final polishing was performed for 300 s with a NX-MET M100 Ø250 polyurethane felt mm and colloidal silica NX-MET XA05 of 0.05 μm mixed with 20 % H_2O_2.

To improve the quality of the surfaces of the samples investigated by SEM-EBSD, an additional super-polishing was performed with a VibroMet2 machine (Buehler Ltd., - USA), using a soft NX-MET M210 felt Ø300 and colloidal silica NX-MET XA05 of 0.05 μm in mixture with 20 % H_2O_2. The device for holding the samples during vibropolishing was 480 g, and the duration of the process was 12 h. Through this operation, the smallest deformations left after the previous polishing were removed, the resulting surface being stress-relieved and with an exceptional flatness.

Before their structural characterization, immediately after vibropolishing, the samples were subjected to chemical attack with a Kroll reagent with the composition: 6 ml nitric acid (HNO_3) + 3 ml hydrofluoric acid (HF) + 91 ml distilled water. The duration of the attack was between 40 and 60 s.

Chemical characterization. The chemical composition of the alloys (TNZT, respectively TNZTSF) in the cast state was determined by the EDS method, with the help of an electronic microscope TESCAN VEGA II e XMU (Tescan - Czech Republic) equipped with an EDS BRUKER Quantax xFlash 6/30 detector. By the same method (EDS), the distribution of the elements (homogeneity) on the surface of the samples was also determined.

Structural characterization. The identification of the phases of the two alloys (in different stages of processing) was carried out by the XRD method using a RIGAKU MiniFlex600 diffractometer (RIGAKU - Japan), in 2 θ, in the range 30 o - 90o, Cu-Kα radiation, (λ~1, 54 Å), with detection limits between 0.1 and 1 % mass / phase.

Microstructure investigations of the as-cast and as-processed TNZTSF alloy were performed using a TESCAN VEGA II e XMU electron microscope equipped with a BRUKER eFlash1000 EBSD detector. The parameters set for the EBSD measurements were: image size – 512 x 512 pixels; EBSD resolution – 320 x 240 pixels; acquisition time / pixel – 10 ms; non-indexed pixel rate less than 2%. During EBSD analyses, the constituent β-Ti phase was indexed in the base-centered cubic (BCC) system with a lattice parameter a = 3.291 Å. Data from EBSD analysis were processed using MTEX Toolbox version 5.7.0 software.

In the case of the TNZT alloy, the microstructure was evaluated by BSE (backscattered electron detector) using the TESCAN VEGA II e XMU electron microscope. All samples were investigated in the RD – ND (Rolling Direction – RD, Normal Direction – ND) section.

Sample preparation for mechanical characterization. For the mechanical characterization through tensile tests of the two alloys, in the cast state and in different stages of processing, samples with the shape and dimensions shown in Figure I.2.11 were obtained by milling. The calibrated portion of the samples had dimensions of 2 x 0.8 x 7 mm. The samples used for the structural characterization were used to measure the microhardness.

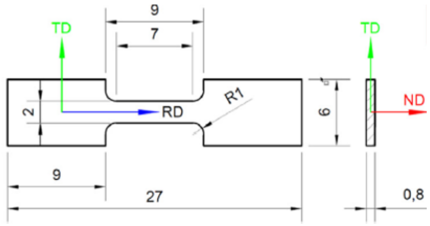

Fig. I.2.11 – *The geometric configuration of the specimens*

Mechanical characterization. The tensile tests (ultimate strength, yield strength, elongation, elastic modulus) were performed using a GATAN MicroTest - 2000N (Gatan Inc. - USA) tension-compression test module, mounted in the TESCAN VEGA II e XMU electronic microscope.

The microhardness of the TNZTSF alloy samples was measured with a Shimadzu HMV-2 microhardness tester (Shimadzu - Japan), by pressing with 100 grams of force for 30 s. For the TNZT alloy, a NNOVATEST Falcon 500 microhardness tester (INNOVATEST Europe BV - The Netherlands) was used, the pressing force being 200 gf, and the pressing time 30 s.

CHAPTER II. DISSEMINATION OF OBTAINED SCIENTIFIC RESULTS

As a result of the running of the experimental programs, in order to fulfil the objectives of the doctoral thesis, the following scientific articles were published with the thesis holder as the main author:

1st Article : **Dan, A.**; Angelescu, M.L.; Serban, N.; Cojocaru, E.M.; Zarnescu-Ivan, N.; Cojocaru, V.D.; Galbinasu, B.M. ***Evolution of Microstructural and Mechanical Properties during Cold-Rolling Deformation of a Biocompatible Ti-Nb-Zr-Ta Alloy***. Materials 2022, 15, 3580. https://doi.org/10.3390/ma15103580 (Factor de impact 3,748);

2nd Article: **Alexandru Dan**, Elisabeta Mirela Cojocaru, Doina Raducanu, Ion Cinca, Vasile Danut Cojocaru, Bogdan Mihai Galbinasu, ***Microstructure and mechanical properties evolution during thermomechanical processing of a Ti–Nb–Zr–Ta–Sn–Fe alloy***, Journal of Materials Research and Technology, Volume 19, 2022, Pages 2877-2887, ISSN 2238-7854, https://doi.org/10.1016/j.jmrt.2022.06.065 (Factor de impact 6,267);

3rd Article: **Dan, A.**; Cojocaru, E.M.; Raducanu, D.; Nocivin, A.; Cinca, I.; Cojocaru, V.D. ***{332}<113> and {112}<111> Twin Variant Activation during Cold-Rolling of a Ti-Nb-Zr-Ta-Sn-Fe Alloy***. Materials 2022, 15, 6932. https://doi.org/10.3390/ma15196932 (Factor de impact 3,748).

The cumulative impact factor for the three articles is 13.763.

CHAPTER III. CONCLUSIONS AND ORIGINAL CONTRIBUTIONS

III.1. GENERAL CONCLUSIONS

The experimental research in this PhD thesis were aimed at developing knowledge related to how the processing by plastic deformation and thermal treatments of some titanium alloys (β-type) intended for bone medical implants contribute to the improvement of their properties.

The following general conclusions can be drawn from the studies and analyses of bibliographic sources carried out within the doctoral thesis:

1. The requirements imposed on metallic biomaterials intended for the manufacture of implants refer to their properties: i) mechanical (tear resistance, yield strength, plasticity, Young's modulus, fatigue resistance); ii) physical (density, magnetic properties); iii) chemical (resistance to various forms of corrosion, degradation through wear); iv) biological (biocompatibility, bioactivity);

2. ***Among the titanium alloys, beta-type ones correspond to the greatest extent to the requirements imposed by applications in the field of implantology*** due to their unique combination of properties (high mechanical strength, low modulus of elasticity, high hardness, good corrosion resistance), which can be substantially improved by heat treatments and plastic deformation (since they have remarkable hot and cold workability, they can be heat treated, the phenomena / transformations that take place during mechanical and thermal processing can be controlled so that the intended properties are obtained) ;

3. ***For metastable beta type titanium alloys***, a low elastic modulus, close to that of human bone can be obtained (thus avoiding the appearance of the "stress shielding" effect), and a high degree of resistance in biological fluids, ***which makes them particularly attractive for biomedical applications***;

4. Nb, Ta and Zr are considered to be the safest titanium alloying elements, this being demonstrated by research studies showing that alloys containing these elements have non-allergic properties, corrosion resistance, tissue/bone compatibility and an availability for cell viability;

7. The mechanical properties of alloys (tear resistance, ductility, toughness, resistance to fatigue and crack propagation) and their corrosion behaviour strongly depend on their microstructure. The metastable Ti-β alloys

consist mainly of the bcc β phase but, depending on the composition and processing method, they may also contain small volume fractions of martensitic phases or the athermal ω phase;

8. The transformation of the microstructure through plastic deformation and heat treatments is done by knowing well the relationship between the microstructure and its properties, it being necessary to design a customized treatment scheme for each alloy.

As a result, *the research strategy in this PhD thesis focused on establishing some processing routes that, through the effect induced by these processings on the microstructures of the investigated bioalloys, lead to obtaining adequate mechanical properties (especially a good ratio between strength and ductility), to allow the use of these biomaterials in implantology*;

9. Considering the above, ***two Ti alloys with original compositions, with non-toxic and non-allergic alloying elements, with a high potential in terms of obtaining biomaterials with advanced properties were designed. These alloys are:***

Ti-32.9Nb-4.2Zr-7.5Ta (% mass) (TNZT);

Ti-30Nb-12Zr-5Ta-2Sn-1.25Fe (% mass) (TNZTSF).

For the two Ti alloys, the parameter that measures the stability of the beta phase, molybdenum equivalence (MoE), is MoE_{TNZT} = 10.15 and MoE_{TNZTSF} = 10.42, respectively. The range of conventional limits for metastable β-type alloys is between 10 and 20 MoE. It therefore results that ***the two TNZT and TNZTSF alloys are of a metastable β type***;

10. *Metastable β-type Ti alloys can undergo structural transformations through complex mechanisms induced by the application of external stress and/or plastic deformation, leading to the formation of stress-assisted, stress-induced, or strain-induced martensite (TRIP), or by a twinning-induced plasticity (TWIP) mechanism.*

In the doctoral thesis, three experimental programs coded TNZT_DP, TNZTSF_DP+TT and TNZTSF_TWIP were developed, which aim to establish the influence on the alloy properties of the chemical composition in correlation with mechanical and thermal processing, the influence of cold plastic deformation on structural transformations, as well as highlighting the transformations structural changes that occur during thermal processing or TWIP processing.

For the experimentation of the three programs, preliminary operations were carried out consisting of: i) the synthesis of alloys, from high purity chemical elements, by melting in a cold crucible furnace; ii) obtaining samples for rolling by cutting from cast ingots.

Sample batches of the two alloys (as cast and processed) were chemically, structurally, and mechanically characterized.

The three experimental programs allow the formulation of specific conclusions derived from the analysis and processing of data resulting from own experimental research.

Cold plastic deformation induces changes in the microstructure and mechanical properties of Ti beta alloys due to the refinement of the crystalline grains and the variation of the participation ratio of the fractions of the constituent phases. These changes evolve with the increase in the degree of plastic deformation; when the degree of deformation increases, the mechanical properties (ultimate strength, microhardness) increase, while the ductility properties decrease.

a) The coded experimental program TNZT_DP aimed at obtaining, through cold plastic deformation, an optimal combination between mechanical strength and ductility of the TNZT alloy intended for applications in the biomedical field. According to this processing scheme, the cast TNZT alloy was plastically deformed by cold rolling with different degrees of deformation: 15%; 30%; 45%; 60%. For the TNZT alloy, processed according to the *codified Experimental Program TNZT_DP*, the following conclusions result:

⁎ the chemical composition determined for the TNZT alloy had values very close to the calculated composition, validating the fact that the synthesis method and process were correctly selected;

⁎ in the metastable β alloy TNZT, a martensitic transformation Ti-β → Ti-α″ takes place;

⁎ the microstructure of the TNZT alloy in the cast state consists of polyhedral β phase grains with an average size of 150 μm in which the Ti-α″ phase with submicron dimensions is dispersed;

⁕ the increase in the degree of plastic deformation causes morphological changes in both the Ti-β phase and the Ti-α″ phase, leading to the development of elongated Ti-β phase grains with acicular Ti-α″ transformed phase content;

⁕ increasing the degree of plastic deformation applied to the TNZT alloy samples leads to a decrease in crystallite size and changes in the weight fractions for both Ti-β and Ti-α″ phases, influencing the mechanical properties of the alloy; ultimate strength and yield strength increase, and the elastic modulus elasticity and fracture strain decrease;

⁕ *by applying to the TNZT alloy a total plastic deformation of 60%, an excellent combination of mechanical properties can be obtained – high fracture resistance (over 1200 MPa), low elastic modulus (50 GPa);*

b) ***The codified experimental program TNZTSF_DP+TT***, aimed at obtaining for the TNZTSF alloy a microstructure with a homogenous equiaxial β -Ti phase, with an average grain size of approx. 60 - 80 μm, with a low residual stress-strain field and a suitable combination of mechanical properties (high strength and ductility, low elastic modulus) has seeked to investigate how mechanical and thermal processing conditions / parameters induce changes on the alloy microstructure. The program consisted of the cold rolling of the TNZTSF alloy in the as-cast state up to a total deformation degree of 50%, followed by solution treatment, at the same temperature (of 850 ^{0}C) but with different holding times (5 min.; 10 min.; 15 min.; 20 min..) - to determine the effect of holding time on the microstructure of the alloy - and then cooling the samples in water. For the TNZTSF alloy processed according to the *codified Experimental Program TNZTSF_DP+TT*, the following conclusions can be drawn:

⁕ the chemical composition determined for the TNZTSF alloy had values very close to the calculated composition, which shows that the synthesis process was the appropriate one;

⁕ the initial microstructure of the TNZTSF alloy, in the cast state, consists of a single homogeneous β -Ti phase, consisting of equiaxed polyhedral grains with an average size of 135 μm, the grain sizes being distributed in a narrow domain;

⁕ plastic deformation by cold rolling with a total applied strain of 50% induces the presence of strain bands, twins and dislocation bands with a high degree of strain texture and preferential alignment of the microstructure along certain crystallographic directions;

⁕ increasing the duration of the solution treatment from 5 min. up to 20 min. leads to obtaining new weakly strained recrystallized equiaxed polyhedral grains showing an average grain size that increases from 60 μm (for a holding time of 5 min.) to 80 μm (for a holding time of 20 min.);

⁕ the evolution of the mechanical properties during cold plastic deformation shows that the strength properties increase while the ductility decreases, due to twin induced plasticity, respectively strain hardening;

⁕ the evolution of the mechanical properties when increasing the holding time for the solution treatment shows that the mechanical resistance properties are decreasing, and the ductility is increasing. This fact is due to the recrystallization phenomenon;

⁕ due to the composition of the TNZTSF alloy (consisting of a sufficient amount of beta stabilizing elements) the formation of α″-Ti and ω-Ti phases is suppressed;

⁕ considering the above, it follows that *by applying to the TNZTSF alloy a cold plastic deformation followed by a solution heat treatment, a suitable combination of mechanical properties (high fracture strength, low elastic modulus and high ductility) can be obtained.*

c) ***The experimental program coded TNZTSF_TWIP*** continued the investigations on the TNZTSF alloy by studying the influence of the intensity of cold plastic deformation on the activation of the twinning systems. Through this program, the as-cast TNZTSF alloy was preliminary plastically deformed, by cold rolling, with a total deformation degree of approx. 35%, after which the rolled samples were subjected to a solution heat treatment at a temperature of 920 ^{0}C for 20 min. and then cooled in water. The alloy samples thus obtained were additionally plastically deformed by cold rolling with different degrees of deformation: 1%; 3 %; 15%. The processing of the TNZTSF alloy according to the *codified Experimental Program TNZTSF_TWIP* has led to the following conclusions:

⁕ the microstructure of the TNZTSF alloy after preliminary cold plastic deformation and solution heat treatment consists of a single homogeneous β -Ti phase, consisting of equiaxed polyhedral grains with an average size of 71 μm, the grain sizes being distributed in a narrow domain;

⁎ during additional cold plastic deformation (with applied deformation degrees of 1 %, 3 % and 15 %) different twin systems can be activated; the {332}<113> system was observed starting from a degree of total plastic deformation of 1%, while the {112}<111> system appears at a degree of plastic deformation of 15%; this shows that the {332} <113> system is the easiest to activate and is the predominant deformation system;

⁎ in the case of the {332}<113> system, variants of primary and secondary twins are observed in the same primary grain, starting from an applied degree of deformation of 3 %.

Considering the results of the characterizations performed on the two alloys Ti-32.9Nb-4.2Zr-7.5Ta (mass %), respectively Ti-30Nb-12Zr-5Ta-2Sn-1.25Fe (mass %) it was found that their mechanical properties, which can be substantially improved by plastic deformation procedures and appropriate thermal treatments, make them very suitable for their use in the manufacture of bone implants. Therefore, for the Ti-32.9Nb-4.2Zr-7.5Ta, the best properties were obtained after cold rolling with a total deformation degree of 60 % (ultimate strength - 1291 MPa, elastic modulus -50 GPa). For the Ti-30Nb-12Zr-5Ta-2Sn-1,25Fe that ws subjected to cold rolling with a total deformation degree of 50%, the resulting properties were: ultimate strength - 1230 MPa, elastic modulus - 58 GPa, elongation to fracture - 8%. After the solution heat treatment, the ultimate strength of the alloy has decreased slightly, concurrently with the decrease of the holding temperature, from 1105 MPa for a holding time of 5 min. at 936 MPa for a holding time of 20 min., but the elongation to fracture has increased (with the increase in holding time from 9% to 15%); the elastic modulus remained relatively constant (58.59 GPa). It therefore results that following the design of appropriate compositions, as well as the application of appropriate deformation and heat treatment processes, two alloys with very high mechanical resistance and a low elastic modulus, and clearly superior properties compared to those of titanium (tear resistance 240 -550 MPa, elastic modulus 110 – 115 GPa) were obtained.

III.2. ORIGINAL CONTRIBUTIONS

Regarding the originality, taking into account the topic addressed - titanium alloys used in bone implantology -, this doctoral thesis contains a series of personal contributions of the thesis holder which are briefly presented in the following:

- Elaboration of a study regarding the field of biomaterials, with an emphasis on the requirements/properties necessary for metallic biomaterials used in the manufacture of medical implants;

- Analysis of the properties of titanium (according to the allotropic state) and titanium alloys (from the point of view of their majority phases), including aspects related to the influence of alloying elements on the final properties of the alloys and on the possibility of their processing through different thermal and mechanic processes;

- Analysis of how the phase transformations specific to titanium alloys take place and the changes these transformations induce in the structure and, implicitly, in the mechanical properties of the alloys;

- A study regarding the conditions required for melting titanium alloys and the influence that impurities (especially gaseous ones) have on the properties of these alloys;

- Knowing that the microstructure has a very important role on the properties of the alloys, a study was carried out on the methods of plastic deformation and heat treatment that can be applied to titanium alloys, including how these processes contribute to changes in the constituent phases and, as a result, of the properties of these materials;

- The design of two Ti alloys, with original compositions, with non-toxic and non-allergic alloying elements, with a high potential in terms of obtaining biomaterials with advanced properties: Ti-30Nb-12Zr-5Ta-2Sn-1 ,25Fe (% mass), respectively Ti-32.9Nb-4.2Zr-7.5Ta (% mass);

- The synthesis of the two alloys in a cold crucible furnace (in levitation), a leading method worldwide in obtaining high-performance biomaterials;

- The development of three original schemes of plastic deformation and thermal treatments, which lead to obtaining for the two titanium alloys of some mechanical properties suitable for their use in implantology (especially a good ratio between mechanical resistance and ductility);

- Investigating how the degree of cold plastic deformation influences the microstructure and mechanical properties of the TNZT alloy;

- Investigating how the conditions / processing parameters of the alloy (cold rolling, solution heat treatment) induce changes in the microstructure and mechanical properties of the TNZTSF alloy;
- Study of the influence of the intensity of plastic deformation on the activation of the twinning systems in the TNZTSF alloy (preliminary plastic deformation by cold rolling, subjected to heat treatment by solution treatment, additional plastic deformation by cold rolling);
- Selection of appropriate methods for characterizing the phenomena/transformation processes specific to titanium alloys as well as their properties, using high-performance apparatus/equipment (SEM, including specific/specialized programs; XRD; mechanical testing mode; microhardness tester).

III.3. FUTURE RESEARCH DIRECTIONS

The steps taken in this research through the study of the two alloys open new perspectives for innovation in obtaining better performing biomaterials that would lead to a longer lifetime of implants, improving patient comfort and reducing costs for drugs and reimplantation.

The two alloys show high potential for their use on an industrial scale in the manufacture of medical implants, which is why further research would be necessary on the refinement of thermal and mechanical processing solutions (with a view to a certain application or a set of applications with specific requirements) and verifying their biocompatibility. In this sense, tests on the characterization of the corrosion behaviour of the two alloys as well as in vitro and in vivo tests are needed to evaluate their biological responses.

In the next period, entities interested in the industrial application of the results of the experimental research carried out in this doctoral thesis can be identified.

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DISSEMINATION

Regarding the dissemination, during the doctoral training cycle the holder of the doctoral thesis, in addition to the three articles contained in the doctoral thesis, the holder of the thesis is co-author in three other articles preset below. Also, the holder of the doctoral thesis participated in three conferences (including one international and two national).

Articles

1. **Dan, A**.; Angelescu, M.L.; Serban, N.; Cojocaru, E.M.; Zarnescu-Ivan, N.; Cojocaru, V.D.; Galbinasu, B.M. ***Evolution of Microstructural and Mechanical Properties during Cold-Rolling Deformation of a Biocompatible Ti-Nb-Zr-Ta Alloy***. Materials 2022, 15, 3580. https://doi.org/10.3390/ma15103580 (Impact factor 3,748);
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