INVESTIGATION THE MECHANICAL PROPERTIES OF POROUS Ti-18Nb-XCu ALLOYS FOR BIOMEDICAL APPLICATIONS

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MASTER THESIS
METALLURGICAL AND MATERIALS ENGINEERING

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I certify that in my opinion the thesis submitted by Muhamad Saad Faaik AL-ABAYHECHI titled “INVESTIGATION THE MECHANICAL PROPERTIES OF POROUS Ti-18Nb-XCu ALLOYS FOR BIOMEDICAL APPLICATIONS ” is fully adequate in scope and in quality as a thesis for the degree of Master of Science

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“I declare that all the information within this thesis has been gathered and presented in accordance with academic regulations and ethical principles and I have according to the requirements of these regulations and principles cited all those which do not originate in this work as well.”

Muhamad Saad Faaik AL-ABAYHECHI

ÖZET

Yüksek Lisans Tezi

BİYOMALZEME UYGULAMALARI İÇİN GÖZENEKLİ Ti-18Nb-XCu ALAŞIMLARININ MEKANİK ÖZELLİKLERİNİN İNCELENMESİ

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Titanyum ve alaşımları, düşük yoğunluk, yüksek mekanik mukavemet, düşük elastik modül, mükemmel korozyon direnci ve iyi biyouyumluluk gibi benzersiz mekanik, fiziksel ve kimyasal nitelikleri nedeniyle tıp alanında yaygın olarak kullanılmaktadır.
Bu çalışmada, farklı konsantrasyonlarda (ağırlıkça %5, 7 ve 9) Cu içeren Ti-18Nb-xCu alaşımları toz metalürjisi (PM) yöntemi ile üretilmiş ve test edilmiştir. Daha sonra bu alaşımlardan en iyi özelliklere sahip alaşıma dört farklı miktarda (hacimce %30, 40, 50 ve 60) tuz (NH_4HCO_3) eklenerek gözenekli numuneler üretilmiş ve test edilmiştir.

Yapılan çalışmalar neticesinde, aynı sinterleme koşulları altında Cu ilavesi sinterlemeyi iyileştirmiştir. Artan Cu miktarı ile genel olarak, basma mukavemeti, sertliği ve rezilyansı artmıştır. Diğer yandan elastikiyet modülünde biraz düşüş gözlenmesi biyomalzeme olarak kullanılması yönünde olumlu bir sonuç olarak kaydedilmiştir.

Sonraki aşamada, alaşımlar içerisinden seçilen Ti-18Nb-9Cu alaşımına farklı oranlarda tuz ilave edilerek üretilmiştir. Bu numunelere de basma, sertlik ve aşınma testleri uygulanmıştır. Bu numunelerde beklenildiği gibi artan gözenek miktarı ile mekanik özellikler ve elastikiyet modülü azalmıştır. Böylece kemik yapısının mekanik özelliklerine yakın olabilecek alaşımlar üretilmiştir.

Çalışmalar neticesinde genel olarak, Cu ilavesi ile Ti-18Nb alaşımının PM metodu ile üretimi kolaylaşmıştır, mekanik özellikler artmıştır. Alaşıma katılan farklı oranlardaki tuz ile açık gözenekli numuneler üretilerek mekanik özellikler istenen seviyelere getirilmiş ve biyouyumluluk yönünden daha uygun alaşım geliştirilmiştir.

Anahtar Sözcükler : Ti alaşımı, Biyomalzeme, Toz metalurjisi, Mikroyapı, Mekanik özellikler, Boşluk tutucu.

Bilim Kodu : 91501

ABSTRACT

Master Thesis

INVESTIGATION THE MECHANICAL PROPERTIES OF POROUS Ti-18Nb-XCu ALLOYS FOR BIOMEDICAL APPLICATIONS

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Titanium and its alloys are widely used in medicine due to their unique mechanical, physical, and chemical properties, such as low density, high mechanical strength, low elastic modulus, excellent corrosion resistance, and good biocompatibility.

In this study, Ti-18Nb-xCu alloys containing Cu at different concentrations (5, 7, and 9 wt%) were produced and tested by the powder metallurgy (PM) method. Then, porous samples were produced and tested by adding four different amounts (30, 40, 50, and 60 vol%) of salt (NH_4HCO_3) to the alloy with the best properties from these alloys.

As a result of the studies, Cu addition improved sintering under the same conditions. The compressive strength, hardness, and resilience generally increased with Cu content. On the other hand, a slight decrease in the modulus of elasticity was recorded as a positive result for its use as a biomaterial.

The next step was produced by adding different amounts of salt to the Ti-18Nb-9Cu alloy selected among the alloys. Compression, hardness, and abrasion tests were applied to these samples. As expected, these samples' mechanical properties and modulus of elasticity decreased with increasing porosity. Thus, alloys that can be close to the mechanical properties of the bone structure have been produced.

As a result of the studies, with the addition of Cu, the production of Ti-18Nb alloy by the PM method has been facilitated, and the mechanical properties have increased. By producing open-pored samples with different proportions of salt added to the alloy, the mechanical properties were reduced to more desirable levels, and the alloy was developed in terms of biocompatibility.

Key Word **:** Ti alloy, Biomaterial, Powder metallurgy, Microstructure, Mechanical properties, Space holder.

Science Code : **91501**

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SYMBOLS

α : Alpha titanium

β : Beta titanium

P : Density

E : Young's modulus

μm : Micrometer

GPa: Gigapascal

MPa: Megapascal

ABBREVIATIONS

PM : Powder metallurgy

ASTM : American Society for Testing and Materials

JCPDS : Joint Committee for Powder Diffraction Standards

Ra : Roughness

EDS : Energy-Dispersive Spectrometry

PART 1

INTRODUCTION

1.1 INTRODUCTION

The field of biomaterials research has expanded due to the ongoing quest for materials that can be used in the human body. Biomaterials for implants must be functional, corrosion-resistant, and biocompatible [1].

Metals are used in the biomaterials of around 70% to 80% of all implants. Metallic biomaterials are essential for healing injured or diseased hard tissues in order to restore function and enhance a patient's quality of life [2].

Conventional titanium alloys $(\alpha + \beta)$ as $Ti - 6Al - 4V$ ELI, as well as cobalt-chromium $(\mathrm{Co} - \mathrm{Cr})$ and stainless steel (Ss), are used in the production of metallic implants nowadays (Extra Low Interstitial) [3]. Titanium and its alloys are increasingly used in biomedical applications due to their higher strength-to-weight ratio, superior biocompatibility, good mechanical properties, corrosion resistance, and low modulus of elasticity compared to other metallic biomaterials like stainless steel and $\mathrm{Co} - \mathrm{Cr}$ alloys [4].

Although the Ti6Al4V alloy is used as one of the primary Ti alloys for biomedical applications, the cytotoxicity of the element vanadium has been reported, and aluminum can influence the development of certain diseases like Alzheimer's disease. Thus, developing alloys that do not contain such elements was necessary to improve the biocompatibility of implants [5].

Inadequate load transmission between implant and bone may cause bone resorption and implant loosening owing to the stress shielding effect; therefore, selecting materials with a low modulus of elasticity, like that of bone, is vital to an implant's success [6].

Increasing the surface hardness of the material is an effective way to improve the wear resistance of a biomaterial, reducing the release of metal ions, which may present cytotoxicity [7]. The ternary alloy Ti13Nb13Zr has in its composition only elements considered biocompatible, it has a lower modulus of elasticity ($\sim$80 GPa) than $Co-Cr$ alloys (~200 GPa), stainless steel (200 GPa), Ti6Al4V (~100 GPa) and Cp $-$ Ti (~105 GPa), and superior corrosion resistance [8].

In the development of implants, doctors and scientists, in general, have encountered problems. Among their mechanical properties, Bones are considered very important, called the modulus of elasticity, or Young's modulus, whose symbol is E. Its corresponding value is between 10 and 30 GPa, which gives them adequate resistance.

In case of damage, they need to be replaced by artificial materials (biomaterials), equally light and resistant, and biocompatible with natural osteoblasts [9]. Biocompatibility was re-defined in 1987 to mean "the ability of a material to behave with an adequate tissue response in a given application" [10].

The biocompatibility of artificial materials is defined within the following: elasticity modules E with values close to the bone E, adequate porosities so that they can establish good junctions with natural bone cells, which are set by embracing the prosthesis by expanding the ramifications of these cells and using them without risk of infection [10].

With research development, the most used materials in prostheses have been stainless steel, cobalt-based alloys (Co), and titanium and their alloys. In this group, Ti and its alloys stand out because of their excellent properties, which are: low modulus of elasticity, low density, high mechanical and corrosion resistance, and superior biocompatibilities when compared to austenitic stainless steel and cobalt-chromium alloys [9].

Considering that the E (elastic modulus) value of Ti (102 GPa) is a higher value than the E of human cortical bone (10 to 30 GPa), there is a difference in stiffness between them and, therefore, the load will not be transferred appropriately to the latter, generating stresses that can shear the bone-implant interface and cause the consequent loosening of the implant [9]. Therefore, even though commercially pure titanium (Cp-

Ti) offers better corrosion resistance and fabric tolerance than stainless steel, its use is limited to specific applications such as pacemakers, heart valves, cages, and reconstruction devices due to its relatively lower strength and unfavorable anti-wear properties [11]. Hence, there is a constant effort in the continuous search for titanium alloys, as the proposal of this work (Ti-18Nb-XCu), in whose samples, after the tests, good mechanical properties can be obtained, improve the redistribution of tension in the adjacent bone tissue, and prolong the life of the prosthesis.

Within the focus of extending the life of the prosthesis, titanium alloys have been developed with lower elasticity modules and free of elements with toxic potentials, such as $Ti - 35Nb - 5Ta - 7Zr$ $(E = 55GPa)$ [12], and, more recently, Ti-35Nb-4Sn (E = 40GPa) with values close to the E of human bone [9, 13]. Titanium alloys are classified based on their microstructure as alloys of the $\alpha, \beta, \alpha + \beta,$ almost α, or almost β type. Ti-Nb binary system (Ti-43Nb, %wt) and an alloy of the $Ti - Nb - Zr$ ternary system (Ti-30Nb-8Zr, %wt) , β-type alloys have received significant attention from the industry and the scientific community in recent years due to their remarkable ability to respond to thermomechanical treatments, and their ability to undergo deformation superior to alloys commonly used by the industry will be addressed throughout all the text.

Compared to their alpha-beta counterparts, beta Ti alloys are easier to work with and have more potential for increased strength, improved notch characteristics (more minor stress concentration effects), and increased toughness during processing. As intended, they may have a lower modulus of elasticity than the $\mathrm{Ti} - 6\mathrm{Al} - 4\mathrm{V}$ alloy (the first generation of Ti alloys produced in the USA) due to the presence of alloy components such as molybdenum, zirconium, niobium, tantalum, and iron (1954) [9, 11].Developing a porous structure in a metal lowers its shear force and elastic modulus. This lessens the stress placed on the tissues around the implant, improves bone-implant interaction, speeds up bone fixing, and enhances the implant's lifespan [9].

There is a great challenge in using titanium alloys, reducing the friction coefficient, which is still very high, with low wear resistance, due to the low hardness and low shear resistance of its oxide surface layer. When this is achieved, together with the young's modulus value, which is already closer to the young's modulus of the human bone, there will be a more excellent resistance to wear, which translates into the achievement of higher hardnesses [9, 12]. Scientists have been working to reduce friction and increase resistance to impact, for example, in surface ceramic coatings (PVD and CVD) or plasma. PVD and CVD mean physical and chemical vapor deposition, but the problem was the higher cost of this technique [14]. Thus, the importance and need to continue technical research work in orthopedics are seen.

In this work, the effect of the niobium and copper content on the mechanical properties of the ternary alloy Ti NbCu in a range of compositions with a constant amount of titanium at 73 wt% and 18 wt.% Nb and Cu content varying between 5,7 and 9 wt% were studied, produced by powder metallurgy from powders and primary mixing method, after different processing conditions and sintering.

1.2 OBJECTIVE OF THE WORK

This work's main objective is to develop a Ti-18Nb alloy by adding Cu to the base alloy. The following steps can summarize this aim:

- Production of Ti-based biomaterials by powder metallurgy method
- Investigate the effect on mechanical properties by adding alloying Cu elements in different ratios (5, 7, 9 wt.%).
- Investigation of the effect on microstructure by adding alloying elements in different ratios.
- Creating open pores in the matrix increases biocompatibility and forms alloys with bone-like elastic modulus.

As a result of these purposes, the main target is; To develop materials with mechanical properties that can be used as bio-materials by using alloying elements with biocompatibility and creating pores in the structure.

PART 2

LITERATURE REVIEW

Ti alloys are used as biomedical implants and devices because they have greater strength and toughness than polymers and ceramics and excellent biocompatibility and stiffness, which more closely resembles human hard tissue. Many studies have been conducted on different aspects of titanium alloys over the last few decades, and this study has led to the development, manufacture, and commercialization of a line of alloys ideal for medical usage. However, further work is needed to improve the performance of these alloys by clarifying critical steps in their production.

In his work, the motivation for the study was twofold. The first motivation concerns the preparation of $\mathrm{Ti}-18\mathrm{Nb}-\mathrm{xCu}$ alloys, where (x= 5, 7, and 9 wt%). The second motivation was the investigation of some mechanical properties, including compressive strength, hardness, and dry wear.

Yoshimitsu investigated the influence of V ions in a culture medium and microstructure, corrosion resistance, mechanical characteristics, and fatigue parameters of $Ti-15Zr-4Nb-4Ta$ alloy in physiological saline solution from 2001 to 2010 [15]. Mitsuo studied the effects of the elements Ta, Nb, and Zr on Ti alloy behavior, leading to the creation of the $Ti-29Nb-13Ta-4.6Zr$ alloy. The specimen's hardness, Young's modulus, and cytotoxicity were evaluated after aging treatments, all of which point to the uniform precipitation of phases throughout. [16]. $Ti-12Mo-5Ta$ alloy was manufactured by D.M.Gordin et al. by melting pure elements in an arc-melting furnace at 950°C for (1 h) under high vacuum before being quenched in water at ambient temperature. They could determine that a novel alloy had a cubic body-centered structure using X-ray diffraction. They also examined the corrosion behavior and Young's modulus of Ringer's solution [17].

The microstructure, phase composition, and shape memory impact of $Ti-16Nb-xSn$ (x = 4.0, 4.5, 5.0 at%) alloys were studied by Wang et al., who found that as

Sn concentration increased, and theβ- phase in the alloys became stable, but that shape recovery ratio decreased as Sn content increased [18]. The corrosion resistance of low modulus Ti16Nb shape memory alloy in Hank's solution at a pH of 7.4 was studied by Y.B. Wang et al. using electrochemical tests. The $Ti16Nb$ alloy performed better than CP Ti in preventing corrosion in Hank's solution. X-ray diffraction analysis of alloy samples revealed that TiO_2 and Nb_2O_5 make up the bulk of the solid phases [19]. Martins used a blended elemental approach, G.V. et al., to manufacture Ti-10, 15Nb alloys from hydride-dihydride (HDH) powders, which were then compressed using uniaxial and cold isostatic pressing before being sintered at temperatures between 900 and 1500 degrees Celsius to achieve densification. X-ray diffraction, scanning electron microscopy, Vickers indentation, the Archimedes technique, and a resonant ultrasound device were used to assess these alloys' hardness, specific gravity, and elastic modulus. The findings revealed the production of phases and the impact of sintering temperatures on the resulting microstructure; the hardness was similar, and the elastic modulus was 18% lower than expected [20]

After that and until 2020, Zhang et al. prepared Ti− Cu alloy by powder metallurgy to estimate antibacterial and mechanical properties. The formed phase was analyzed by XRD and SEM/EDS techniques. The hardness, compressive strength, and corrosion resistance were tested compared to cp-Ti [21]. Ti_2Cu was the primary, secondary phase in all Ti-Cu alloys. In contrast, the Cu-rich phase was generated in the alloys with 5 wt.% or more copper, according to research by Jie Liu et al. In order for $Ti - Cu$ alloys to have strong and stable antibacterial activities, the Copper concentration must be at least 5 wt.%, and the Copper-rich phase is thought to play a crucial role in the high antibacterial activity seen in these alloys [22]. In a study by Maria et al., a ternary $Ti - 15Zr - 10Nb$ alloy was shown to have novel microstructural and mechanical characteristics and outstanding long-term corrosion resistance in solutions mimicking physiological conditions. Optical microscopy and Scanning electron microscopy showed a biphasic + Widmanstatten microstructure with distinctive interleaving lamella and phases. The mechanical characteristics of the alloy are comparable to those of titanium, with Young's modulus of 64 GPa, which is near to the human bone, and greater ultimate tensile strength, suitable 0.2% yield strength, and strain to fracture to those of Ti-alloy. Films of TiO_2, ZrO_2, and Nb_2O_5 oxides 5.5 ±0.5 nm thick are present in the alloy's natural state to provide protection [23]. Mutlu et al. produced porous

$Ti– Nb– Cu$ alloy by a PM method. The addition of Nb was done to stabilize the β-Ti phase, while copper addition improved the sinterability and lowering the sintering temperature of the alloy. Electrochemical corrosion behaviour was done, and compression was tested [24]. Mechanical parameters, including tensile strength, elongation after fracture, yield strength, and Vickers hardness, were studied by Masatoshi et al. for the $-6\%Nb - 4\%Cu, Ti - 18\%Nb - 2\%Cu, and\ Ti - 24\%Nb - 1\%Cu$ alloys. The Ti-6%Nb-4%Cu sample was monophasic in α-β phase, whereas the $Ti - 18\%Nb - 2\%Cu\ and\ Ti - 24\%Nb - 1\%Cu$ samples were biphasic in - and -phases, respectively. Tensile strength, yield strength, and hardness improved over $Ti - 5\%Cu$ and $Ti - 30\%Nb$ while breaking elongations were reduced [25]. Eren Yilmaz and colleagues used Particle-in-Molecule (PIM) technology to create $Ti - 16Nb - XSn$ (X:0, 2, and 4 wt%) alloys. The Elastic Modulus was reduced from 128 GPa to 77 GPa by adding 2% Sn to the base alloy; however, it was noted that no reduction was feasible by increasing the quantity of the Sn. The hardness was between 4500 and 8000 MPa, and the sintering temperature range was from 1250 to 1400 °C [26]. The morphology and structural characteristics of αtype $Ti - 15N$b alloys were assessed by XRD analysis after preparation and sintering at temperatures of 800, 900, 1000, and 1100 °C by Fellah et al. Young's modulus, hardness, and relative density of $Ti - 15Nb$ alloys were all improved with increased sintering temperature. As a further step toward tribological characterization, wear performance was examined utilizing a ball-on-plate type Oscillating tribometer at varying applied different loads $(2, 8, and\ 16\ N)$ [27]. Microstructural, corrosion, mechanical, antibacterial, osseointegration and cytotoxic, and characteristics of a powder metallurgy-prepared nanocrystalline Ti-Cu intermetallic alloy showed the production of $TiCu$ and Ti_2Cu_3 as main phases with a grain size of 23 nm, as reported by Javadhesari et al. The synthesized alloy has a toughness of 8.14 MPa.m$^{1/2}$ and a hardness of 10 GPa [28]. Chang Bo Yi et al. studied the corrosion resistance, antibacterial properties, and mechanical properties of $Ti - xCu$ alloy ($x = 2, 5, 7, and\ 10\ wt.\%$) by Ar-arc melting method following by heat treatment. The results showed that the precipitated phases were mostly β-Ti matrix and Ti_2Cu phase, and that the copper element accumulated in the lamellar structure to form the precipitated Ti_2Cu phase. The elastic € and compressive strength changed as the amount of Cu increased. Compared to other $Ti - Cu$ alloys, the $Ti - 7Cu$ alloy had a maximum compressive strength (2169 MPa) and a low elastic modulus E (108 GPa) [29] . To gauge the mechanical incompatibility with human bone, Akira et al. developed a $Ti-15Nb$ alloy using arc melting. The cytotoxicity was tested both directly and indirectly using the MTT assay, and the Vickers microhardness and elastic modulus were also examined. No cellular morphological differences were detected, and strong adherence was seen across all experimental settings [30].

Using the powder metallurgy technique (at 950 °C for 6 h), Jassim et al. recently concentrated on producing low modulus β-Ti-based alloys for biomedical applications. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) were used in the characterization process, and several mechanical parameters were also examined (Brinell hardness, compression, and elastic modulus). High mechanical and wear qualities were found for solutions containing 2 wt% indium particles, which were tested for corrosion resistance in Hanks and saliva [31].

PART 3

THEORETICAL BACKGROUND

This chapter presents a theoretical foundation on titanium and its alloys, covering the general aspects of its use as a metallic biomaterial. An overview of Titanium-Niobium alloys, as utilized in implants and bone grafts, is presented in this chapter. Some current research and studies will be included in the discussion of titanium alloy chemical formulations, which include biomaterials and mechanical characteristics as well as styles of titanium alloys and the phase diagram of Ti-Nb alloy.

3.1 BIOMATERIALS

Biomaterials are artificial or naturally occurring substances that mimic the properties of biological tissues. Developing novel materials suitable for this use is the subject of significant research and development activities. Biomaterials science is the branch of science that examines the physical and biological studies of materials and their interactions in the biological environment in an interdisciplinary way. The relationship of biomaterials science with other disciplines is shown in Figure 3.1. Biomaterials science; examines the production, optimization, characterization, test methods, and tissue-material interaction of biomaterials and other related disciplines [32].

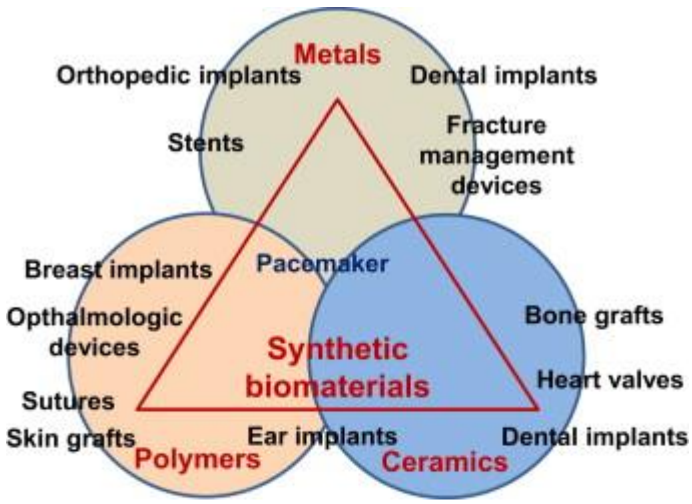


Figure 3.1 The relationship of biomaterials science with other branches [32].

Although the science of biomaterials has been applied since the history of humanity, it is a new field in the scientific sense. The best example is organs such as the nose, eyes, and teeth used artificially in Egyptian mummies. The use of gold in dentistry dates back two thousand years. In the 19th century, the rate of implants used in the body began to increase. In 1880, ivory was used as a prosthesis and placed inside the body. In 1938, vitalium was produced as the first metal prosthesis, and over time it was exposed to high metal corrosion, posing a danger to living organisms. In recent years, ceramic, metal, and polymer materials have regenerated different body parts. For instance, the replacement of blood vessels in the 1950s, hip replacements in the 1960s, and synthetic sutures in the 1970s [33]. As a result of the developments in recent years, biomaterials are used for diagnosis and treatment to fulfill the function of organs that have lost their function and are damaged, help heal damaged tissues, and increase the functionality of many organs. Examples include bone screws and suture threads, dialysis machines, artificial heart and pacemakers, implants, eye lenses, probes, interaction, and probes [33]. The loss of function of organs and tissues due to diseases, traumas, and accidents caused by any reason reduces the quality of life considerably.

Since traditional treatment methods (autograft, allograft, xenograft) are insufficient to cure the diseases, the most compatible biomaterials are required for tissues that have lost their function [34]. According to their effects on the living body, biomaterials are classified as bioactive, toxic, bioinert, and tolerant. The bioactive effect is the name given to the biomaterials that enable forming similar cells in the applied tissue. Many materials used in the medical field are used after being subjected to many tests and approved for biocompatibility. Despite all the precautions taken, the biomaterial may have carcinogenic, allergic, mutagenic, immune, non-immune, and inflammatory effects on the human body.

For this reason, the test results are significant [35]. The toxic effect may directly or indirectly disrupt the body's structure and cause undesirable situations due to placing the biomaterial in the body. In this case, the body shows different reactions and shows that the toxic effect occurs.

The bioinert effect can be combined with bone tissue and biomaterial without limited fibrous tissue. Biomaterial and tissue are to interact with each other. The bioinert effect is mentioned if the applied tissue and the biomaterial do not interact. The tolerant effect is that the biomaterial is surrounded by fibrous tissue in the area where it is applied. The tolerant effect is seen in many materials.

For the design of biomaterials, biomedical engineers, pathology and clinical therapists, and materials science engineers must work in collaboration. The choice of biomaterial is determined by the type of medical application that will take place.

Biomaterials in different human body parts; artificial heart valves can be used as stents in blood vessels, knee, ear, shoulder, hip, wrist, and dental prostheses [36]. The biomaterials used in the human body are shown in Figure 3.2.

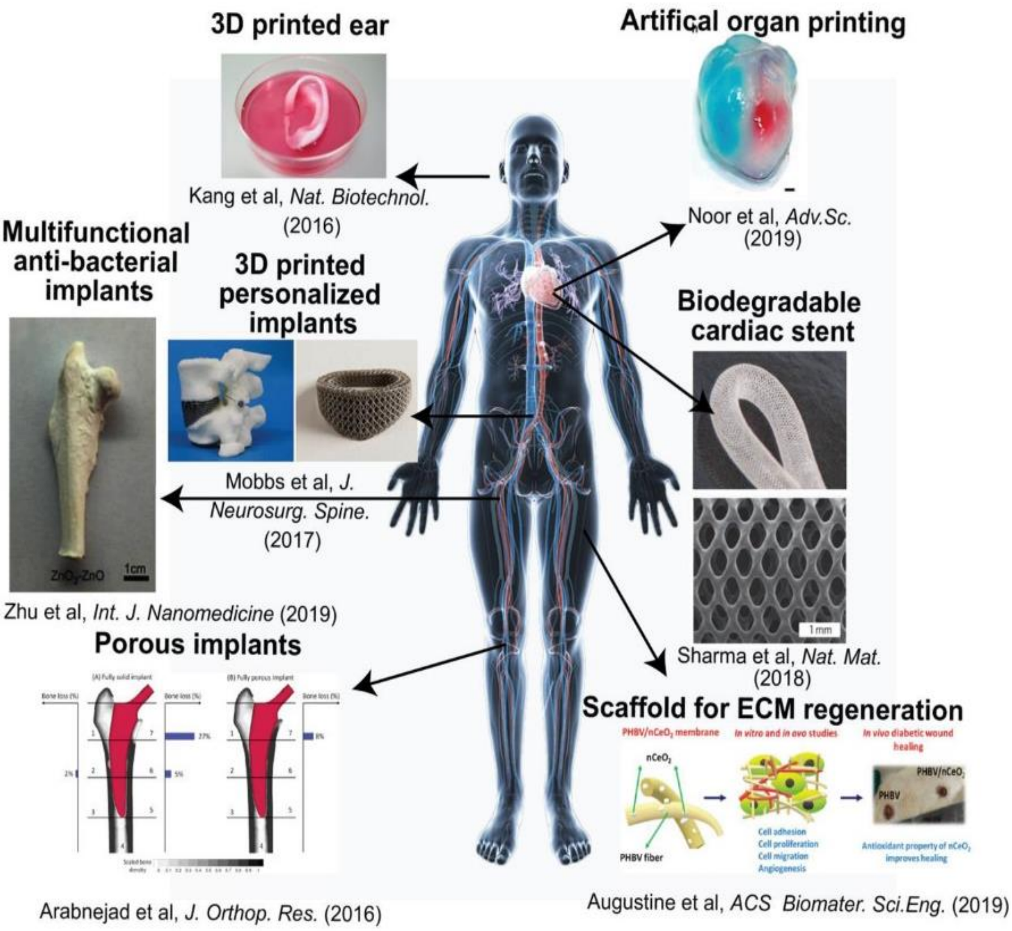


Figure 3.2 The use of biomaterials in the body [36].

Biomaterials are used in the human body for temporary and permanent purposes. Provisional applications are placed in the human body and taken in short- and short-term applications. Surgical equipment, screws, plates, and wires for fixation in bone fractures are examples of temporary applications. Permanent applications are long-term applications placed in the human body and undertake the functions of tissues and organs. Teeth, spinal cages, joint implants, aneurysm rings and latches, heart stents, and screws are permanent applications [37].

3.2 BASIC PROPERTIES OF BIOMATERIALS

Assuming the functionality of any tissue and organ, the biomaterials used in the human body must have some fundamental properties not to damage the surrounding tissues. Basic properties such as biocompatibility, resistance to chemical effects and corrosion, good mechanical properties, elastic modulus close to the bone, and appropriate design are required [38]. In order to last for a more extended period, without rejection and maintaining its functionality, a biomaterial must have the following attributes.

3.2.1 Biocompatibility

Biocompatibility involves the acceptance of an implant by neighboring tissues and the living organism as a whole. Materials intended for use in the medical field must be biocompatible if they are not to cause any harm to the surrounding biological structures, including aberrant inflammation, allergic reactions, or immune system responses.

Excellent mechanical qualities, good optical properties, and appropriate density are other compatibility criteria that may be significant in the operation of an implant. For an implant made of a biomaterial to be successful, it must first be accepted by the body [36].

Instead of tissue and organ losses that occur, materials with high biocompatibility are used in the human body. When the implants are placed in the body, they either fully comply with the tissue or reject them by showing incompatibility or keeping them in the body by showing complications. The expected feature of the biomaterial is that it is permanent in the body without causing complications [34].

3.2.2 Bioactivity

The bioactive material is the name given to materials that can interact with tissues and is also preferred by cells in the body [36]. For example, bioactive glass-ceramics (Cerabone), A/W glass-ceramic, machinable glass ceramics, bioglass, dense hydroxyapatite (Durapatite, Calcite), bioactive composites (Polyethylene-

Hydroxyapatite, HAPEX). It is a common feature of bioactive glasses and glass ceramics to form a biologically active hydroxy carbon apatite (HCA) layer with collagen fibers. The HCA layer positioned on the implant is physically and chemically equivalent to the structure of the bone. This equivalence is also the reason for connecting at the interface [39].

Bioactivity is the state of physical solid bond formation and integration that occurs at the interface of the biomaterial with the tissue. On the other hand, bioactive materials show good interaction and combination due to a biological reaction between the biomaterial and the tissue [40].

3.2.3 Mechanical properties

Mechanical characteristics such as tensile strength, hardness, modulus of elasticity, and elongation are crucial. The material's response to repeated cycles of load or stress is crucial to the long-term functionality of an implant subjected to cyclic loading. When an implant breaks because the bone and metal are not mechanically compatible, this is known as biomechanical incompatibility [6]. Bone's elasticity modulus ranges from around 4 to 30 GPa, with the exact value dependent on the bone type and the direction of the test. The current implant materials are more stiff than bone, which reduces the transmission of stresses between the bone and implant, leading to bone resorption and eventual implant loosening. Read about the stress shielding effect for more information on how mechanical incompatibility leads to bone cell death. Therefore, materials with a high strength-to-weight ratio and a modulus of elasticity close to that of bone are recommended.

3.2.4 Corrosion and wear resistance

Implants in the body have poor corrosion and wear resistance, which may release components that might induce unfavorable responses in the body, such as allergies and toxic reactions. Low wear resistance can also result in implant loosening, and wear debris can deposit on tissues, causing various reactions [6].

Tissues and organs in the human body are active environments that will provide high corrosion conditions to metals. For this reason, it is desired that the materials used in biomedical fields have very high corrosion resistance.

3.3 METALS AS BIOMATERIALS

Metals are used as biomaterials because of their excellent mechanical characteristics, resistance to corrosion, thermal conductivity, and electrical conductivity, as well as their simplicity of manufacture and low cost. Some metals are used in hard tissue replacement, such as complete hip and knee joint prostheses, bone plates and screws, spinal fixation devices, and dental implants to help repair fractures [36].

Most metallic elements, such as $Cr, Fe, Ni, Co, Ta, Ti, and\ Mo,$ used in the manufacture of implants can be tolerated by the body in limited quantities. However, metallic elements are not accepted by the body in high amounts, which raises some concerns about the biocompatibility of metallic implants since they are subject to corrosion in the in vivo environment, as well as wear, which results in the release of metallic ions.

316L stainless steel, cobalt-chromium ($Co - Cr$) alloys, and titanium and its alloys are presently employed as surgical implants. However, owing to the corrosive action in the body environment, the elements cobalt, chromium, and nickel are liberated from stainless steel and $Co - Cr$ alloys [41]. Due to the toxicity of nickel, considered a toxic and even carcinogenic element, skin diseases such as dermatitis have been reported, and animal studies have shown carcinogenicity due to the presence of cobalt [42].

Metals are used in biomaterial applications due to their physical properties to provide functionality and desired additional properties to the material. The usage areas of metal alloys in biomedical applications are given in Table 3.1.

Table 3.1 The use of metal alloys in the biomedical field [43].

Implant	Example	Type of metal
Neurological	Neuromodulation device Recording electrodes Cochlear implant	Ti; $Ti6A14V$ Pt; W; $Ptlr$; $316L\ SS$ $Pt\ Pt$
Cardiovascular	Stents Artificial valve Pacemaker, ICD Catheters	$316LSS$; $CoCr$; $CoCrPt$; Ti; $PtCr$; $Ti6A14V$; $TiNi$; PtW; $Ptlr$ $316L\ SS$; $Ti6A14V$; $CoCrMo$ Pt; $Ptlr$; Ti $316L\ SS$; Pt; Ti; $TiNi$; $Ti6AL4V$
Orthopedic	Bone fixation (plate, screw pin) Artificial joints Spinal rods	$316L$; Ti; $Ti6A14V$ $CoCrMo$; $Ti6Al\ 4V$; $Ti6A1Nb$ $316L\ SS$; $CoCrMo$; Ti; $Ti6A14V$
Dentistry	Orthodontic wire Orthodontic brackets Fillings Restorations	$316LSS$; $CoCrMo$; $TiNi$; $TiMo$ $316L\ SS$; Ti $AgSn(Cu)Hg\ amalgam$; Au $Au-Pt-Pd-Ag$; $Au-Pt-Cu-Zn$
Craniofacial	Plate and screw Cranial plates Orbit reconstruction	$316L\ SS$; $CoCrMo$; Ti; $Ti6A14V$ $316L\ SS, Ti$; $TiNi$; $Ti6A14V$ $CoCrMo$; Ti; $TiNi$; $Ti6Al4V$
Otorhinology	Artificial eardrum	316L SS
Gynecological	Intrauterine devices	Cu; CuAg (Nova T380)

While one of the most significant applications of metallic materials in implants is the replacement of bone that has suffered wear or damage, a significant disadvantage is the difference between the mechanical behavior of implants made of conventional materials and bone [44].

Thus, among the range of materials available for application as implants, the selection of materials based on titanium and its alloys occurs because they present better characteristics such as high strength, high corrosion resistance, low density, lower modulus of elasticity, in addition to not show cytotoxicity [6]. Figure 3.3 shows the elastic modulus of different alloys used as implants.

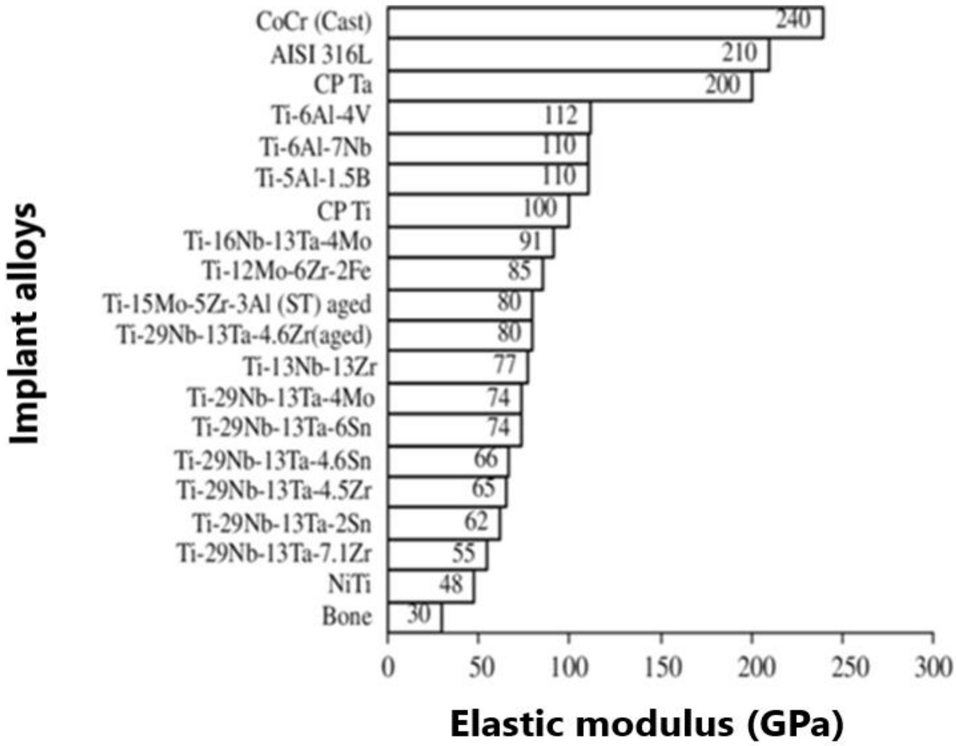


Figure 3.3 Elastic modulus of different alloys used as implants [45].

It is desired that metallic biomaterials are highly corrosion-resistant, compatible with tissue, not deteriorating, not causing toxic and allergic effects, and biocompatible. The implants are desired to be attached to the bone cells by adhesion force in the body. Another desirable property in metallic biomaterials is metallic fatigue or Young's modulus. In order to keep the prices at a lower level, surface treatments (such as polishing, processing, etc.) should be done quickly. Another essential feature is applicability in medical equipment and implant production and optimization stages. According to the types of metals and alloys used in the application, stainless steel ($DIN/ISO\ 5832-1\ or\ AISI\ 316L$), $Co-Cr$ alloys ($DIN/ISO\ 5832-4\ or\ DIN/$

$ISO\ 5832-6$), CP-titanium ($DIN/ISO\ 5832-2$) and titanium alloys (DIN) /($ISO\ 5832-3$) and CP-niobium and CP-tantalum [26].

Metallic biomaterials are classified according to metal and alloying elements. The most commonly used pure and alloys are metallic biomaterials, alloys of $Ti, Cr, Co, W, V, Al, Ni, Mo,$ and stainless steel. Metals are rarely used alone because of their insufficient properties. However, the improvement of its properties with the addition of alloying elements has made their use widespread and convenient. Stainless steels, titanium-based alloys, and cobalt-chromium alloys are metal groups used in orthopedic surgery. The most commonly used metallic biomaterials, $Ti-Al-V$ alloys, are pure titanium and stainless steels with $Co-Cr-W-Ni, Co-Cr-Mo, and\ Co-Ni-Cr-Mo-Ti.$

The first metallic biomaterial is a stainless steel 18/8 Cr/Ni alloy produced as an implant. Such biomaterials are produced from vanadium steel because they have high corrosion resistance and good durability. When vanadium steel was used alone as an implant, it could not be used in vivo for a long time due to insufficient corrosion resistance. It has been observed that the corrosion resistance of the 18/8 Mo stainless steel against the brine solution increases by increasing the % Mo ratio by one part, and this alloy is named ASTM 316 (American Society For Testing And Materials) stainless steel. This alloy was re-formed in 1950 by reducing the amount of carbon in the stainless steel from 0.08% to 0.03%, and it was found to have better resistance to the saltwater solution. The stainless steel produced in this way with low carbon is called ASTM 316 L steel.

Stainless steels have low biocompatibility and cannot be fully incorporated into bone or soft tissue. For example, microscopic fibrous tissue forms between the stainless steel and the bone, close to the bone in the body. This limits the use of stainless steel in applications where implant success is dependent on tissue compatibility and integration. The most commonly used steels in implant production are 316 and 316L stainless steels [46].

It is desired that the fatigue strength of the implants used in the human body is good. We can understand the importance, mainly if an implant is used in hip connections. Assuming that a healthy person takes one million steps per year, it is predicted that this person's hip connections will be weighed two or three times his body. This situation has prevented cast stainless steel in orthopedics due to its low fatigue strength and coarse grain size. The most useful in stainless steel is low carbon 316L. However, it should not be overlooked that stainless steel cannot be used in all areas due to the poor compatibility between texture and metal [47].

Cobalt-chromium is the most widely used cobalt alloy for biomaterial purposes. It has high elastic modulus, hardness and strength values , and high corrosion resistance compared to stainless steel. It has weaker properties in terms of formability and ductility. The most commonly used are cobalt chromium-molybdenum and cobalt-nickel-molybdenum alloys. Cobalt-chromium-molybdenum in artificial joint and dental applications; Cobalt-nickel molybdenum is mainly used in hip, knee, and joint prostheses working under load.

Nickel-titanium alloys, which deteriorate and return to their original shape when affected by heat, are called "shape memory alloys"; Vascular connections in the skull, orthopedic prostheses, dental bridges, and muscles for the artificial heart are the applications in which the use of this alloy is preferred [48].

Titanium and its alloys started to be used in biomaterials towards the end of the 1930s due to their lightness compared to stainless steel and cobalt alloys. Its superior biocompatibility and non-toxic effects cause titanium to be among the most widely used metals.

3.4 TITANIUM AND ITS ALLOYS

The tenth most prevalent element in the crust of the planet is titanium. Although titanium is more readily available than copper and iron, it is used in structural applications 200 times more often than copper and iron each year [49].

Due to their high biocompatibility, specific (mechanical resistance-weight), and corrosion resistance, titanium, and its alloys offer the best combination of properties required for biomedical applications, setting them apart from other metallic materials used as biomaterials like stainless steel and $Co - Cr$ alloys. Titanium-based biomaterials and related alloys are widely used in hard tissue replacement, such as hip replacement implants and dental pins [7]. To prolong the implant's life and prevent bone resorption, the modulus of elasticity of the implant must be close to that of the bone. Pore introduction and microstructure control are two ways to reduce the modulus of elasticity in titanium alloys.

Although the elastic modulus can be easily controlled by varying the porosity content, having its value reduced as the pore content increases, and an appropriate pore size provides a better induction of bone growth, the mechanical strength has its value reduced drastically. Additionally, it is known that pores are important nucleation points of fatigue cracks that can lead to failure, reducing the useful life of the biomaterial [50].

At room temperature, pure Ti appears in the α-phase with a hexagonal compact crystal structure (HCP), which allotropically transforms at 882°C into the β $-$phase, body-centered cubic (BCC) [6, 36].

The inclusion of alloying elements tries to keep the α or β phase stable. The nucleation and development of the β phase from when the material is cooled is the basis for the microstructural modification of titanium alloys by heat treatments. When the β phase is quickly chilled, the martensitic transition is conceivable. There are two kinds of martensite:' α' (compact hexagonal) and α" (orthorhombic) [51].

Stabilizing elements of the α phase are aluminum, oxygen, nitrogen, and carbon, which act by increasing the β transition temperature. β-phase stabilizing elements lower the β transition temperature and are classified as isomorphic or eutectoid. The isomorphs are: molybdenum, vanadium, niobium, tantalum, and tungsten, and the eutectoids are: iron, chromium, silicon, nickel, cobalt, copper, and manganese. There are also neutrals, such as zirconium and tin [6]. Figure 3.4 presents different schematic types of phase diagrams for Titanium alloy [52].

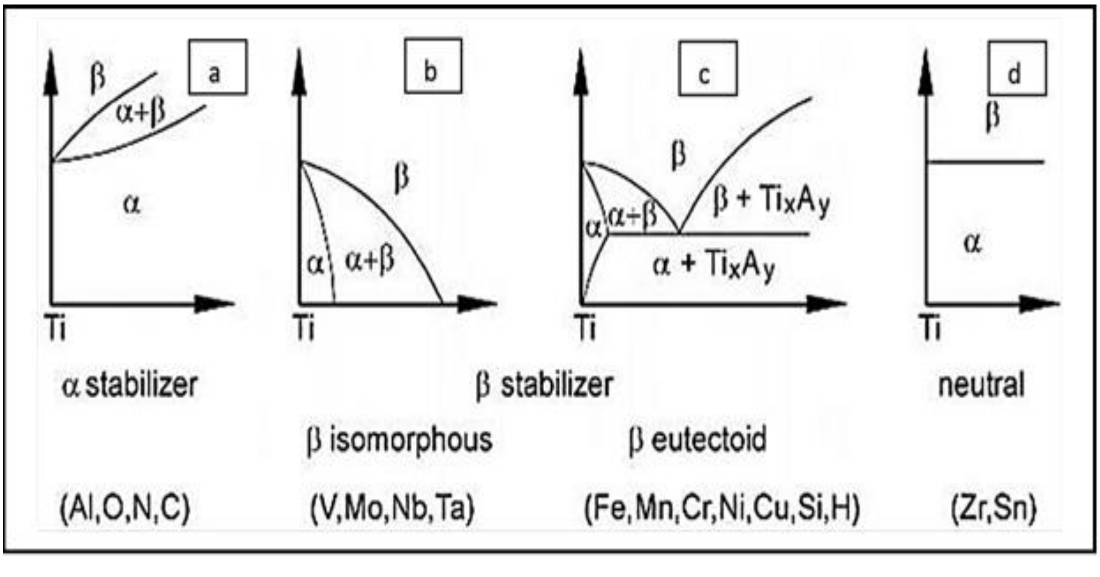


Figure 3.4 Different types of phase diagrams for Titanium alloy [52].

According to the amount of α and β phases present, alloys can be classified as α alloys, near α alloys (near-α), α + β alloys, near β alloys ($near - \beta$), and β alloys [53]
The α alloys are those in which any retention of the β phase at room temperature is impossible, even in metastable form. The presence of α-phase stabilizing elements, such as solute in the titanium matrix, elevates the $\alpha/\alpha + \beta$ and $\alpha + \beta/\beta$ transformation lines, causing, even if the alloy is cooled in the α+β field, the portion phase is always to the left of the Ms/Mf line at room temperature, being thermodynamically unstable, transforming into α.
Near-α alloys contain α-phase stabilizing elements but present β-phase stabilizing elements in small amounts. The presence of β −phase stabilizing elements in the α alloy, even in small amounts, makes the expansion of the α + β field sufficient to allow a small amount of β-phase to be retained at room temperature in metastable equilibrium, allowing the martensitic transformation of the β phase into α' (HC structure martensite) within a minimal range, obtained through high cooling rates, from the α + β field. Such alloys contain 1 to 2% β stabilizers and 5 to 10% β phase [6].
α+β alloys contain one or more α-stabilizing elements added to one or more β-stabilizing elements. These alloys are formulated so that the α phase (HC) and the β phase (CCC) coexist at room temperature with an amount of β phase between 10 and 50%. Near-β alloys are alloys with β-phase stabilizing elements in sufficient quantity for the martensitic transformation lines to pass below room temperature and for the $\alpha + \beta/\beta$-transit line to be well below the allotropic transformation temperature of the pure titanium. These alloys may have low levels of α-phase stabilizing solutes, thus working within the β field at 800 °C. The kinetics of nucleation and growth of the α-stable phase is relatively slow, allowing the maintenance of the metastable β-phase at room temperature without rapid cooling.
β alloys are alloys with concentrations of β-phase stabilizers sufficient so that only this phase is in thermodynamic equilibrium at room temperature or with nucleation and growth kinetics of α so low that there is no occurrence of α or α +β, predominating the β phase after conventional heat treatments. However, in commercial β alloys, there is always some degree of α precipitation during aging [6].
The α and near-α alloys exhibit superior corrosion resistance, but their low mechanical strength limits their application as an implant device. Alloys with α+β microstructure

exhibit high mechanical strength due to the presence of the two phases [54]. Type β and near-β titanium alloys have high mechanical strength, good formability, and hardenability. These alloys offer a low modulus of elasticity with superior corrosion resistance. Alloy design associated with thermomechanical processing control has allowed alloys to be produced for implants with optimized properties.

Although the α and β phases, in isolation, present low mechanical strength, the α/β interfaces constitute an efficient barrier to dislocation movement and the propagation of cracks within the α or β grains. The distribution of the primary α phase exerts the most significant influence on the mechanical properties. When it is in the form of platelets (or Widmanstätten), it is particularly favorable to mechanical strength but detrimental to the alloy's ductility. When its morphology is equiaxed or globular, it is generally beneficial to tensile ductility but reduces mechanical strength [54].

The secondary α phase, obtained by aging, directly influences the level of mechanical strength. The fine precipitation of this phase inside the β grains significantly increases its value, and the fine dispersion of these phases inside the β grains directly affects the fracture toughness and ductility of the alloy.

However, due to the wear and corrosive action, it is subjected to in the body environment, vanadium and aluminum ions can be released from the Ti64 alloy in the body. Due to the cytotoxicity of vanadium and studies that associate neurological disorders with aluminum, new β-type titanium alloys composed of non-toxic and non-allergic elements were developed [6, 7]. As α+β alloys have high elastic modulus values, resulting in bone resorption and implant loosening, alloys that retain large amounts of β-phase during cooling are of great interest. Theoretical studies carried out by Song and collaborators showed that Nb, Zr, Mo, and Ta are the alloying elements most suited to reducing the modulus of elasticity of the β phase of Ti without compromising strength.

The $Ti-13Nb-13Zr$ alloy is a $near-\beta$ alloy developed in the early 1990s for orthopedic applications due to its low elastic modulus and composition with only non-toxic elements [55].

Niobium acts as a β-phase stabilizer, and despite its neutral behavior, studies carried out by Geetha et al. showed that the addition of zirconium contributes to stabilizing the β phase in the $Ti-Nb-Zr$ ternary system [6].

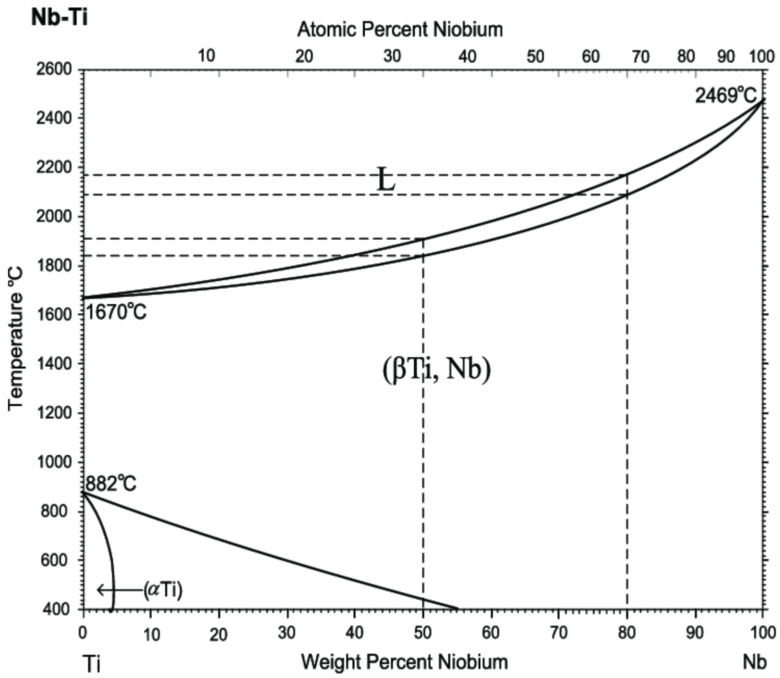


Figure 3.5 Binary phase diagram of $Ti - Nb$ alloy [6].

Due to the precipitation of refined grains of β-phase during the aging treatment, the microhardness of the alloy is increased, and the modulus of elasticity is proportional to the quantity of -phase present in the alloy. In contrast, refined grains are not necessarily linked to a rise in strength and modulus of elasticity.

3.5 MECHANICAL PROPERTIES OF TITANIUM AND ITS ALLOYS

3.5.1 Resistance limit

Among the metals, titanium is the material that has the best mechanical strength/weight ratio. The specific masses of titanium alloys vary between 4.43 g/cm^3 and 4.85 g/cm^3, and the tensile strength limit can vary from 500 MPa, for commercially pure titanium, to 1500 MPa for β alloys. Hardened for the $\alpha + \beta$ intermediate alloys, there is a value of around 900 to 1300 MPa [56]. The influence can explain this almost three-fold difference between the maximum and minimum values that alloying elements and heat treatments exert on the mechanical properties of titanium and its alloys. The chemical composition determines the volume of α and β phases. The α-phase is less ductile and more difficult to deform than the β-phase, which has a body-centered cubic structure due to the limited-slip systems of its hexagonal close-packed crystal structure. The tensile strength can be considerably increased through heat treatments, as the microstructural aspects that most affect this property are associated with aging processes by β-phase precipitation or martensitic quenching. The aluminum in the α phase in ternary systems, as in the case of the Ti-6Al-4V alloy, introduces a solid solution hardening effect, but the interaction of the α and β phases achieves a significant increase in strength. The magnitude of this effect depends on the nature and structure of the two phases and, mainly, on the heat treatments to which they are subjected [57].

3.5.2 Ductility

The most significant influence on ductility is linked to the resulting microstructural variation when processing the alloy preferentially in the β field than in the α+β field. The reduction in fracture area of $\alpha + \beta$ alloys is halved when processed in the β field. This reflects the substantial increase in microstructural unit size resulting from rapid grain growth in the β field. The systematic study of $\alpha + \beta$ alloys showed that the reduction in grain size eliminates nucleation voids and, consequently, increases ductility [58]. Rare earth additions also produce increased ductility [59]. Quenching to produce martensite reduces ductility and does not always increase strength. The aging treatment aimed at improving mechanical strength also results in loss of ductility [60].

3.5.3 Fracture toughness

For a wide range of titanium alloys, fracture toughness can be increased by using a suitable heat treatment, starting from the β field, which allows for obtaining a microstructure that contains the α phase in the form of platelets or precipitates [61]. The α/β interfaces are essential in the fracture course. However, the advantages gained from processing in the β field may be lost if the cooling rate is high enough to produce martensite, which reduces toughness. Air cooling or oil quenching is used industrially [62]. When a crack crosses colonies of α-phase plates of parallel orientation, the individual interfaces between the plates, even if they contain thin β layers, may not be efficient in stopping the crack propagation. Thus, the crack will only undergo deflection when it changes from one colony to another, and, at this point, a substantial crack deflection may occur in the plane of maximum stress, contributing to the increase in toughness. The mechanical properties of titanium and its alloys can also strongly influence the cold working and grain size [63].

3.6 NIOBIUM AND ITS STRATEGIC ROLE

Charles Hatchett discovered niobium in 1801, naming it columbium when he separated it from the mineral columbite. Years later, the German chemist Heinrich Rose, unaware of Hatchett's work and thinking he had found a new element by separating it from tantalum, named it niobium in honor of Niobe, daughter of the mythological King Tantalus, who was officially adopted. By the International Union of Pure and Applied Chemistry only in 1950.

Until the end of the 1950s, niobium was obtained as a by-product of the treatment of columbites and tantalites, minerals that are not very abundant, which implied a high price and restricted use in the production of a particular type of stainless steel and some superalloys. With the discoveries of significant pyrochlore reserves, especially those in Araxá-MG, and given the technical feasibility in the early 1960s, a radical transformation took place in the scenario of supply, prices, and availability in the markets.

Among the critical and strategic minerals, niobium is of great importance in the Brazilian scenario, mainly due to its properties and applications in the high technology industry and defense material, combined with the fact that Brazil holds the largest reserves in the world.

In titanium alloys, niobium is a very efficient β-stabilizing alloying element. Ti alloys containing up to 15% by weight of Nb and subjected to sudden cooling allow obtaining an essentially martensitic structure of the acicular α' (hexagonal) type. When increasing the content to values between 17.5 and 25% by weight of Nb, the rapid cooling leads to the formation of α" (orthorhombic) martensite. Using values close to 27.5% and quickly cooling the microstructure of this material, it consists of metastable β-phase, making it possible to obtain a structure consisting of stable β-phase using levels above 30% [64].

Figure 2.6 shows the behavior of a binary Ti-Nb alloy in terms of its modulus of elasticity after sudden cooling from a temperature of 900°C. Compositions with 15 and 43% Nb content by weight are the compositions with the lowest modulus of elasticity [65].

Analyzing the Ti-Nb phase diagram Figure 3.5 and the elastic modulus values, it is observed that if the alloy contains solid solution β, its elastic constants decrease, proportional to the numerical relationship between the phases α and β. This also indicates that the solid solution β, which has a BCC structure, has a lower elastic modulus than the solid solution α, which has a compact hexagonal structure [65].

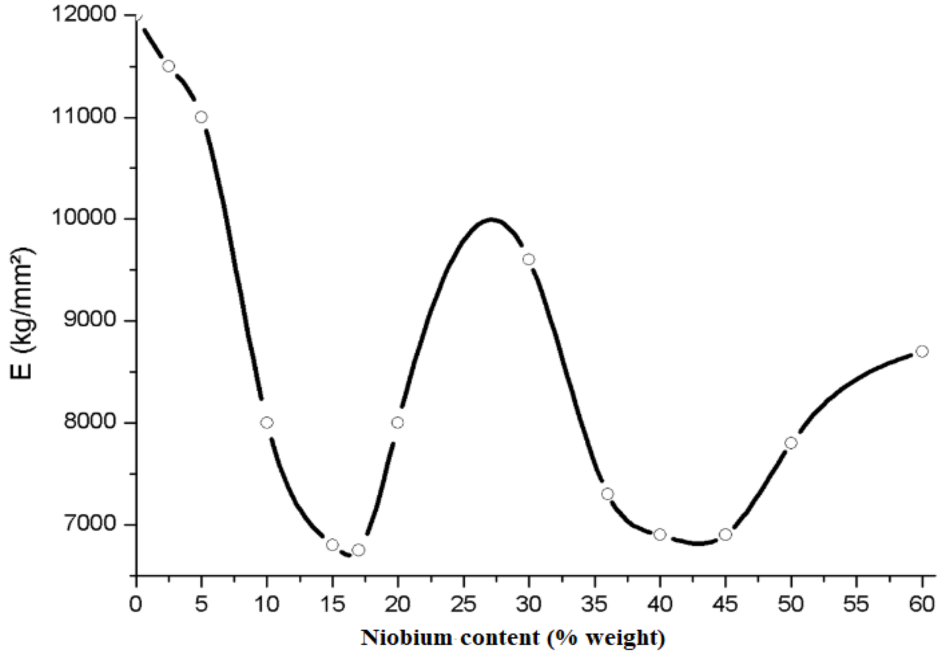


Figure 3.6 Relationship between elastic modulus and Nb content in the binary Ti-Nb alloy after sudden cooling from a temperature of 900°C [65].

3.7 TITANIUM POWDER METALLURGY

Titanium alloys have a very high machining cost. Powder metallurgy (PM) is a cost-effective method because it may create components with a final form that is very close to the intended ("near-net-shape") [55].

Powder metallurgy produces metallic or ceramic compounds through powder production and consolidation by applying pressure and heat at temperatures below the melting point of the principal constituent [66]. Physical and chemical methods can obtain the powder. Among the existing methods, the following can be mentioned [66]:

- The reduction of oxides is a chemical process based on the equilibrium of reduction reactions that use hydrogen, carbon monoxide, and carbon.
- Hydrometallurgical process – a chemical process consisting of the ore's leaching, followed by the precipitation of the metal in the solution. Precipitation can occur directly by electrolysis, cementation, and chemical reduction or indirectly by precipitation of hydroxides, carbonates, and oxalates.

- Thermal decomposition of carbonyls is a chemical process in which carbonyls are obtained by reacting the metal with carbon monoxide under specific pressures and temperatures and, soon after, heated to form the metal.
- Metallic hydration is a process in which the metal is hydrogenated, forming brittle hydrides, ground, and dihydride under vacuum and high temperatures.
- Atomization is a physical process that breaks a liquid into tiny droplets with diameters smaller than 150 μm. A disturbing flow must enter the collision process with the molten metal. Droplets from the collision are formed, turning dust through rapid cooling. Depending on which medium or process is used to produce the droplets, atomization can be classified into gas atomization, water atomization, centrifugation, and vacuum atomization.

The relevant aspects for obtaining the powder are average particle size, morphology, and chemical composition. Following the obtaining of the powder, the grinding process takes place. In this impact, friction, shear, and compression forces act on the larger metallic particles, promoting their breakage by micro forging, fracture, agglomeration, and deagglomeration, reducing the size—particle average. After milling, the forming step follows, based on the compaction of the powder contained within a rigid matrix or a flexible mould through pressure [67].

The two basic types of pressing are uniaxial, in which pressure is applied in a single direction, and isostatic, in which pressure is applied uniformly across the entire surface of the mould containing the particulate material through the application of fluid—pressurized [68].

According to the powder used as the starting material, titanium alloys produced by M/P can be classified into three categories: pre-alloyed Ti alloys, rapid solidification, and elemental mixing [59]. The use of alloys produced by blending elemental powders effectively reduces the cost of the final material due to the low prices of titanium elemental powders and other elements. Commonly used titanium powders include titanium sponge fines and titanium powders produced by the hydrogenation-hydrogenation process [59].

Using the powder metallurgy technique, it is possible to produce and design materials with a porous structure and produce dense implants with high strength. There are two structures, porous and dense, considering the bone structures. The powder metallurgy technique ensures that the implants used in dentistry applications are produced in a porous structure with features suitable for bone. For example, Ti30Ta alloy is preferred in the cortical bone because it has an elastic modulus close to the bone and a pore amount of 15-20%. Bone-compatible titanium alloys such as Ti15Mo5Zr3Al, TMZF, Ti13Nb13Zr, Ti6Al7Nb, and TNZT are also produced by powder metallurgy technique and offered for use. The production of these alloys, which are compatible with bone, using the powder metallurgy technique, leads to the formation of alloys with a wide range of product portfolios and mechanical properties by following different conditions for different situations. This situation enabled the production of parts with desired properties by preferring superior aspects of mechanical or physical properties in different applications.

Processing titanium alloys via powder metallurgy involves two basic steps: powder production and compaction/sintering to form the final part [55].

3.8 COMPACTING OF THE POWDERS

Compaction is the first stage of part consolidation, in which the powder is subjected to compression forces due to the simultaneous displacements of the upper and lower punches [69]. Checking the final dimensions, or approximately the final dimensions of the part, and guaranteeing the necessary mechanical resistance for later handling, are the main objectives of this step.

In short, it is possible to divide the behavior of the powders when submitted to compression into three stages [70]. First stage: The particles of the different powders are reorganized, thus avoiding the formation of voids. Second stage: Plastic deformation of the particles occurs, which is related to the ductility of the powder. The compressibility of the powder depends on its plastic deformation capacity. Generally, powders with porosity (those produced by reducing oxides) have low compressibility. Third stage: The powder particles that have become brittle due to the hardening process fracture, forming smaller fragments. Uniaxial cold pressing is one of the most used compaction methods. At room temperature, the powder is poured into the mold cavity, after which the upper punch applies pressure in the vertical direction due to penetration into the mold cavity. In the end, the part is removed due to the upward movement of the upper punch.

In addition to the pressing, there is cold isostatic pressing, which uses Pascal's principle as a mechanism. At room temperature, the pressure acts uniformly on the mold inside a pressure vessel, which homogeneously compresses the powder. The main advantages of this process are high resistance to green and superior specific mass when compared to uniaxial cold pressing. On the other hand, in hot isostatic pressing, isostatic pressure is combined with applying high temperatures in a mold, capable of deforming due to heat. In this process, obtaining the highest densification rates with fully dense compacts is possible. The compaction cycle must be organized so that the tension in the affected area is uniformly distributed [71]. Figure 3.7 shows compaction pressure's influence on the compacted section is green density [72].

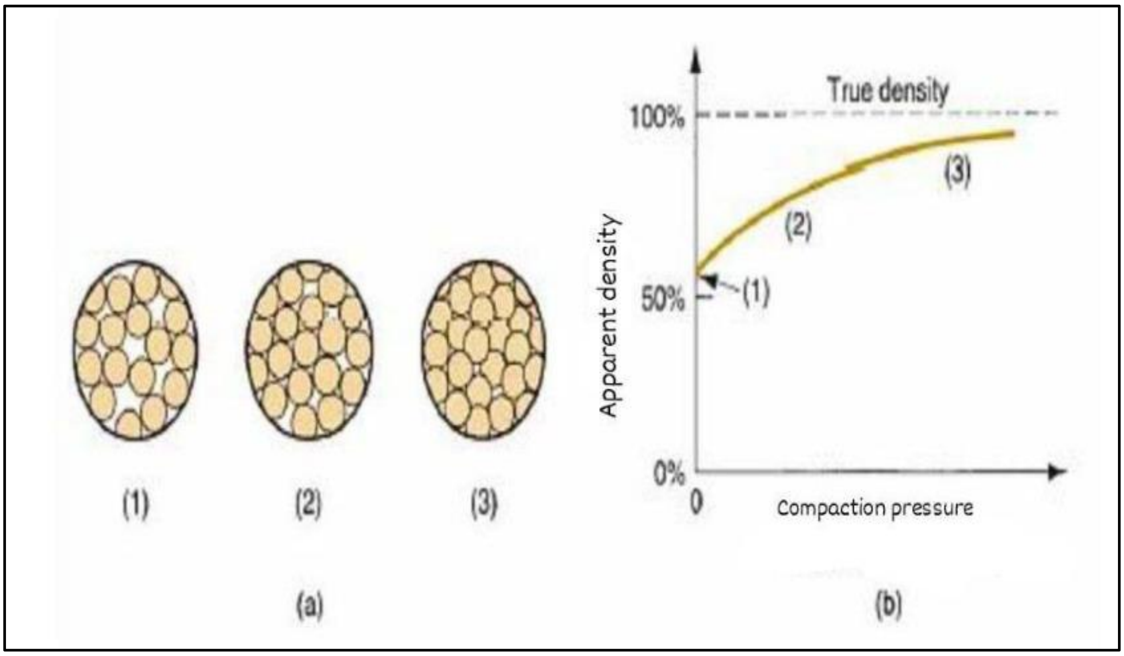


Figure 3.7. (a) Effect of pressure on particles arrangement during Compaction; (b) Density of the powders as a function of compaction pressure [72].

3.9 SINTERING PROCEDURES

Sintering is a heat treatment responsible for bonding particles through mass transport, preferably in the solid state. The connection promotes an increase in mechanical strength and a decrease in the system's energy [73]. Pores are eliminated as the particles unite during sintering, and the process temperature generally corresponds to 2/3 of the material's melting temperature [74]. The driving force of sintering is the decrease in surface free energy caused by the decrease in the total surface of the particles. The reduction of the total surface occurs by the disappearance of the material/pore interface, which is replaced by the material/material interface when the porosity disappears [75]. Powders with smaller granulometry have high surface energy; due to this, the sintering process takes place faster or at lower temperatures.

Furthermore, reducing atmospheres can be used in sintering, aiming at the following objectives [76]:

- Prevent air from entering the furnace and reacting to the atmosphere. - Facilitate the removal of lubricant or wax from the compacts.
- Reduce the oxides present on the surface of the powders.
- Supply chemical elements to the sintered sample.
- Transmit heat uniformly and efficiently.

In solid-phase sintering, mass transport takes place without any liquid phase present. It is customary to divide this process into three stages, as shown in Figure 3.8.

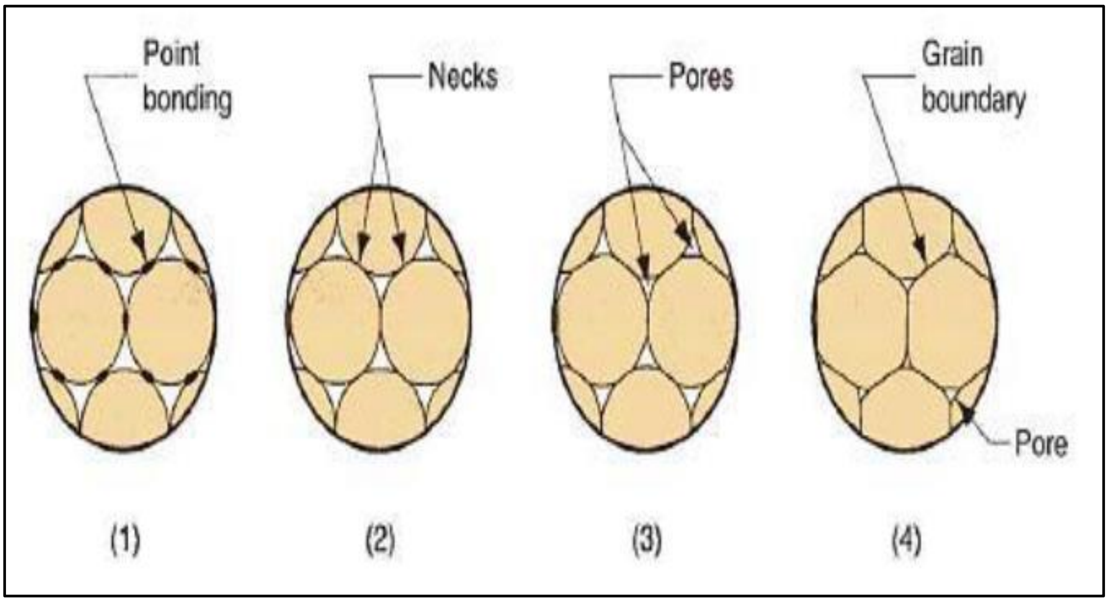


Figure 3.8 Illustration of the sintering stages: (1) initial part, (2) initial stage (forming necks), (3) intermediate stage, and (4) final stage [72].

In the first stage, contact between particles occurs due to the diffusion of atoms, with the consequent formation and growth of “necks.” As the process continues, new “necks” are formed, where they begin to interfere with each other [72]. During the intermediate stage, the neck radius/particle radius ratio increases, causing the particle identity to change. This stage is responsible for the densification of the compact and the decrease in pore diameters. Due to this decrease, many pores come into contact, forming a network of pores throughout the volume of the piece.

Consequently, there is an increase in the continuity of the matter and a reduction in the volume of the pores, producing shrinkage in the volume of the sintered part. The isolation and rounding of the pores characterize the final stage of sintering. These are closed, losing their original shape, allowing them to reach theoretical density values between 90% and 95%. Gases inside the pores limit the piece's final densification. On the other hand, liquid sintering occurs with a liquid phase during the process, usually due to the melting of one of the alloying elements. This technique reaches maximum densification with minor residual porosity. In addition, it is responsible for giving the materials excellent mechanical properties.

3.10 BIOMEDICAL APPLICATIONS OF TITANIUM AND ITS ALLOYS

The fatigue strength of metallic biomaterials must be high enough to withstand the stresses of regular usage. Hard and wear-resistant ceramic biomaterials find widespread usage as articulating surfaces in joints and teeth and bone-bonding surfaces in implants. Articulating surfaces made of polymeric materials are typically flexible, stable, and low-friction. Due to its many desirable features, titanium is quickly rising to the ranks of the most promising engineering materials. Its use in mechanical and tribological components is attracting increasing attention in the biomedical field [77].

Several characteristics make titanium alloys principles in orthopedic prosthesis manufacturing and dental application :

• In body fluid, titanium alloys with superior corrosion resistance

•Less modulus elasticity, about (50%-60%) of that competing cobalt- based super alloys.

•Best mechanical strength and small density are the reason for high specific strength [78].

These days, titanium alloys are the most sought-after metals for use in the medical field. They have a broad range of applications in medicine, including load-bearing device manufacture for the orthopedic and dentistry industries and implant devices that mimic the properties of crash hard tissue. Examples include knee and hip replacements, bone plates and screws for fracture repair, artificial hearts, and replacement heart valves [79, 80]. One of its essential uses is the replacement of worn or injured joints to restore lost human bone structures and functions [81]. Alloys ($Ti-6Al-4V$) and ($Ti-6Al-7Nb$) are two of the most extensively utilized implant materials, notably in dentistry, orthopedic, and osteosynthesis applications. [82]. Titanium alloy $\mathrm{Ti-6Al-4V}$ has been used extensively in the medical field. However, the alloy may have a toxic effect due to free vanadium and aluminum, making it unsuitable for permanent implant applications. Consequently, alternatives to titanium-aluminum-vanadium ($Ti-6Al-4V$) implants have been developed for various medical implant settings. One of the new alloys is called $\mathrm{Ti-6Al-7Nb}$ ($ASTM\ F1295$), and other examples include $Ti-13Nb-13Zr$ ($ASTM\ F1713$) and $Ti-12Mo-6Zr$ ($ASTM\ F1813$) [80] .

3.11 POROUS MATERIALS IN BIOMEDICAL APPLICATIONS

Porosity is a defining characteristic of porous materials [83]. Based on the synthetic materials used to generate them, porous materials may be classified as either porous metallic or porous non-metallic materials (e.g., ceramics and plastics). Depending on the geometry, porous metals may be divided into closed-cell and open-cell structures. A closed-cell structure has isolated cells separated from one another by a thin wall or metal matrix, as opposed to the interconnected cells of an open-cell structure [84]. Numerous desirable properties of metals may be traced back to their porous interior structure. Possible properties include low heat conductivity (for closed-cell structures), high energy absorption, radiation ability, high heat exchange, high permeability (for open-cell structures), and good absorption of electromagnetic radiation (for bone regeneration, heat resistance, heat shock, and so on). As a result, porous metals have been used in various applications where strength and functionality are required. They have been used as building materials, heat exchangers, substitutes for hard tissues, absorption buffers, and more.

Orthopedic surgery is complicated by differences in the host bone's and metallic implants' Young's moduli and inadequate osseointegration. Two significant load transfer changes occur once a metallic implant is placed in the intramedullary canal of the bone. First, the load is transmitted via the implant-bone junction, not the bone.

Second, the implant shares the bone's burden—the stem shields the bone from stress, causing bone resorption. Low osseointegration slows implant fixation. Bobyn et al. [85] studied stem stiffness and stress-related bone resorption. Cobalt-based and titanium-based porous-coated femoral implants were put in eight dogs. After death, stem designs were evaluated for bone ingrowth and remodeling. The femora with a less rigid titanium alloy stem lost less bone than the stiffer one.

Titanium and its alloys experience stress shielding because their elastic modulus values are lower than other metallic implant materials but greater than bone. One possible solution to this issue is constructing the stem out of a porous material.

3.12 PORE-FORMING AGENT METHOD

Because of titanium's high melting point, reactivity at high temperatures, and expensive manufacturing costs, various solid-state processes for fabricating porous titanium structures have been developed. Powder metallurgy (PM) technology has recently been used in several solid-state foaming processes.

A space holder strategy, comprised of solid elements that may be removed throughout the production process, is used to manufacture porous Ti for structural or biological purposes. The manufactured porous metals have two kinds of pores: isolated micropores scattered in the wall of the interconnected macropores and interconnected macropores. This method begins with mixing pure or alloyed Ti powder with a suitable space-holding material, which is then compacted into a preform. The preform is then sintered in a vacuum at a low temperature (about 200°C) to remove the space holder and create porosity in the titanium. This stage also results in the creation of the first neck. Sintering at higher temperatures (1200-1400°C) results in neck growth, leading to metal matrix structure densification. Powder space holder materials used to manufacture porous titanium or its alloys include carbamide ($CO(NH_2)_2$) [86], magnesium, ammonium hydrogen carbonate (NH_4HCO_3), and polymers such as polypropylene carbonate (PPL).

Bram et al. [87] stated that titanium was used to produce highly porous components using carbamide. The space holder was dampened with a solvent on a rolling bench, and metal powder was added to the mixture to attach to the surface. The agglomerates were uniaxially compressed at 166 MPa. Thermal treatment below 200°C removed the space holding material, then sintering the compacts between 1200° and 1400°C in a vacuum furnace for 1 to 2 hours. 60-77% porosity was reached with 0.1-2.5 mm pores.

Compressive and bending strengths were 10 MPa and 100 MPa for 77% and 60% porosity, respectively. Niu et al. [86] recently fabricated porous titanium utilizing carbamide as a space-holder and three heat treatments (200°C for 3 hours, 350°C for 3 hours, and 1250°C for 3 hours), reaching porosities of 55-75%. Plateau stress and Young's modulus were 10-35 MPa and 3.0-6.4 GPa, respectively.

Wheeler et al. [88] employed magnesium powder as a space-holder in porous Ti-6Al-4V and Ti structures. The magnesium spacer holder was removed by evaporating at 1000oC and sintering at 1400°C, resulting in 25-82% porosity, 15-607 MPa strength, and 3-9 GPa Young's modulus. Esen and Bor [89] a magnesium powder in the 425–600 m particle size range that can be sintered in a single step to produce porous titanium foam. Using a 500 MPa compactor, combine titanium powder, binder, and space holder; heat to 1200 °C for 1 hour to accomplish debinding, sintering, and magnesium evaporation; cool. Porous titanium (45–70%) had a yield strength (plateau stress) of 15–116 MPa and an elastic modulus of 0.42–8.8 GPa.

Wen et al. [90] used ammonium hydrogen carbonate to create a 78% porous titanium lattice. Heat treatment at 200°C and sintering at 1200°C for 2 hours decomposed the space holder. Compressive strength was 35 MPa, and Young's modulus was 5.3 GPa. Further research [91] yielded 35-80% porous titanium. Plateau stress and Young's 80% porous titanium modulus were 40 MPa and 2.87 GPa. After thermochemical processing, the porous titanium formed a bone-like apatite layer [92].

This process generated porous titanium alloys with high porosity and strength [93, 94]. Porous titanium alloys' bioactivities were also examined. Similar to the previous procedure, space holders make porous titanium alloys (sintering of powder compacts). Starting ingredients were mostly mechanically-alloyed powders. Wen et al. [91] heat-treated pre-alloyed TiZr alloy powder and the space holder at 200°C for 5 hours and 1300°C for 2 hours, resulting in a 70% porous TiZr alloy. Porous TiZr alloy has 78.4 MPa compressive plateau stress and 15.3 GPa Young's modulus. Wang et al. [94] effectively synthesized a porous $Ti-10Nb-10Zr$ alloy with porosities between 42-74%. Porous TiNbZr has more muscular strength (27-368 MPa) than porous unalloyed titanium. Cell cultures on the porous alloy revealed osteoblast-like cells developed throughout.

Xiong et al. [95] porous TiNbSn was discovered to have similar bioactivity and mechanical properties. By adjusting the initial space holder to the TiNbSn powder ratio, porous TiNbSn products with four distinct relative densities were fabricated. Ball-milled TiNbSn alloy powder and a space holder were subjected to heat treatment at 175oC for 2 hours before being sintered at 1200^{o}C for 3 hours, resulting in the porous alloy. For a porous TiNbSn alloy, the plateau stress in compression ranged from 112 to 420 MPa, and Young's modulus was 10.8 to 33.2 GPa. A porous TiNbSn alloy surface pretreated with alkali heat treatment grew hydroxyapatite when doused in SBF. The results demonstrated the bioactive potential of the porous alloy.

Despite the development of porous pure titanium and titanium alloys, the makeup (pore placement) of the initial pores in the powder preform typically determines the shape and the porosity level of the subsequent porous pure titanium and titanium alloys based on the space holder approach. After the completion of sintering at high temperatures, the pore shape and porosity level cannot be modified using this method.

3.13 SUMMARY

Over time, biomedical materials have seen tremendous advancement. Medical device and prosthesis development have led to the creation of several metals with improved biocompatibility and corrosion resistance. Some biomaterial applications may benefit more from the broader features metallic biomaterials provide. Hip and knee prostheses, plates, screws, and dental implants are all examples of metallic biomaterials utilized as structural materials in places with significant applied stress. Metallic biomaterials should fulfill the following primary criteria: biocompatibility; biomechanical compatibility (appropriate Young's modulus and compressive strength); osseointegration; and viable processing, including manufacturability, serializability, and availability. While stainless steel and cobalt-based alloys have traditionally been employed as metallic biomaterials, titanium and its alloys are becoming more popular because of their superior corrosion resistance, biocompatibility, low elastic modulus, and high strength-to-weight ratio.

In comparison to Ti-29-67 13Ta-4.6Zr's GPa elastic modulus and robust heat treatment response, $Ti-35Nb-7Zr-5Ta$ has the lowest Young's modulus at 55 GPa. To make a titanium alloy stronger, it may be aged at low temperatures, where the martensitic phase will precipitate within the phase. Young's modulus for $Ti-24Nb-4Zr-7.9Sn$ ranges from 33 to 42 GPa. The elastic modulus of bone could be comparable to that of these alloys due to their high porosity. Porous materials may also promote osteoblastic cell adhesion and osseointegration. Due to titanium's high melting point and chemical reactivity, porous titanium alloys are best produced using solid-state foaming based on powder metallurgy instead of liquid foaming. CP titanium powder and/or pre-alloyed powders are used as raw materials. Common titanium alloys with aluminum and vanadium have a porous structure that makes them biocompatible, but this rigidity comes at a cost and complicates the manufacturing process. The pre-alloyed powder is what adds the extra cost. Biocompatible elemental powders as base materials might be the answer to these issues.

The present study investigates a manufacturing strategy for $Ti - 18Nb - XCu$ and porous $Ti - 18Nb - 9Cu$ alloys employing a solid-state technology; mixing, alloying, and foaming biocompatible elemental powders using salt as a space holder.

PART 4

METHODOLOGY AND EXPERIMENT

4.1 INTRODUCTION

This chapter details the experimental work and explains how the experiments were conducted. Equipment and materials used in this investigation are included. The experimental procedure used to prepare samples starts with mixing powders; compacting and sintering process has been presented. All mechanical and physical tests are also presented in this chapter. These tests include density, porosity, compression, young modules, micro-hardness, X-ray diffraction, scanning electron microscope analysis (SEM), Energy-dispersive analysis (EDS), and the wear test.

4.2. PROGRAM OF THE PRESENT STUDY

In the current study, Table (4.1)-coded samples were created, where the matrix alloy is based on ASTM F 2066-08 [96]. Figure (4.1) summarizes the overall program used in the present work.

Table 4.1. Prepared Samples in the Present Study

	Ti	**Nb**	**Cu**	**Salt**
Samples without salt				
Ti-18Nb	82	18	0	-
Ti-18Nb-5Cu	77	18	5	-
Ti-18Nb-7Cu	75	18	7	-
Ti-18Nb-9Cu	73	18	9	-
Samples with salt				
Ti-18Nb-9Cu+30	73	18	9	Vol%30
Ti-18Nb-9Cu+40	73	18	9	Vol%40
Ti-18Nb-9Cu+50	73	18	9	Vol%50
Ti-18Nb-9Cu+60	73	18	9	Vol%60

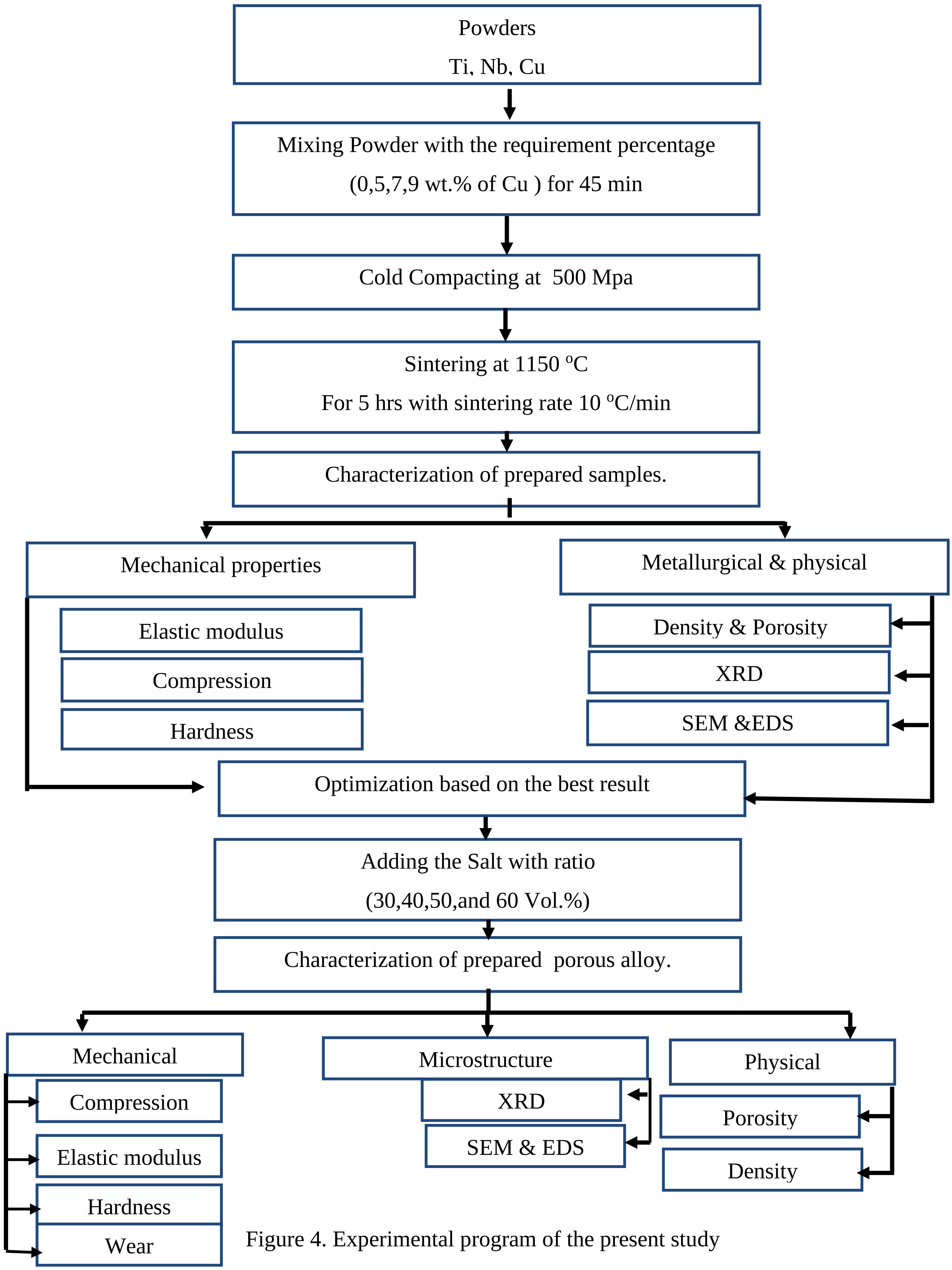
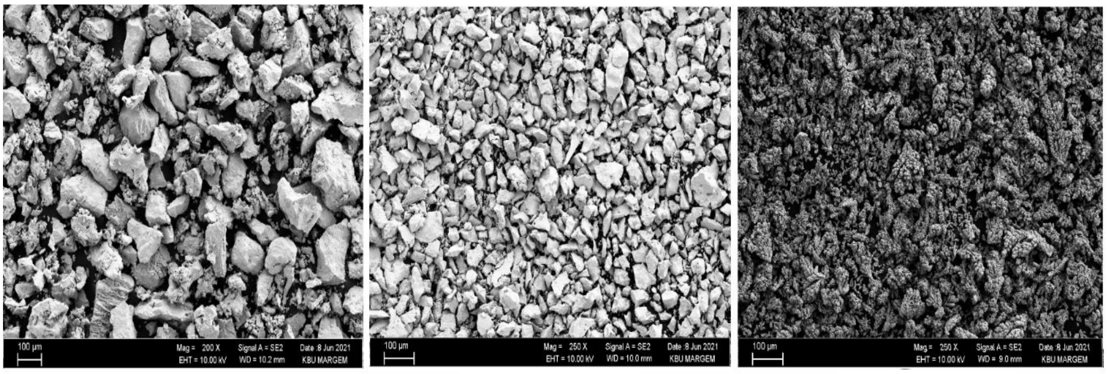


Figure 4. Experimental program of the present study

4.3. MATERIAL

The Ti-18Nb-xCu alloys were prepared through the cost-effective blended elemental PM method. Adding 5, 7, and 9 wt% of copper to a Ti-Nb alloy allowed researchers to see how the metal's presence altered the material's characteristics. Ti-18Nb was maintained as the basic alloy, and a rise in Cu content was countered by a fall in Ti. In Fig. 4.2, we see the elemental powders used: Cu (sponge powder, purity >99.5), Nb (99.8%), and Ti (99%).



Ti Nb Cu

Figure 4.2. The general view of the elemental powders.

4.4 PREPARATION METHOD

For this experiment, we used a 3D shaker mixer (Turbula) to combine elemental powders with varying salinity levels (1 hr). The powder mixture was pressed in a cylindrical steel mold (13 mm in diameter) at room temperature using a uniaxial press without any lubricant or binder. The samples were compressed at $450, 500,$ and 600 MPa; the 500 MPa pressure was ultimately chosen (see Fig. 4.3). For the sintered (5 hr) and cooled (5 hr) green samples, the Protherm PZF cylindrical tube furnace was used at $1150\ ℃$ at a speed of $10\ ℃/\mathrm{min}$ under Ar gas (Fig. 4.4).

Figure 4.3. The sample's pressing, mold, and diameter.

Figure 4.4. The tube furnace was used in this work.

The cut samples for the microstructural study were ground with SiC paper (240 - 1200 p), polished with 6µm diamond, and etched with 5% Nital in that order.

4.5 MICROSTRUCTURE CHARACTERIZATION

4.5.1. X-ray diffraction (XRD)

X-ray diffraction investigation was performed on sintered samples (13 mm in diameter and 3 mm in height). The measurement circumstances are (Target: Cu, a wavelength of 1.54060Å, voltage, and current of 30 kV and 15 mA, respectively, scanning speed (2 degrees per minute), and scanning range (10 - 90 degrees)). The matrix alloy phases and reinforced particles were determined using X-ray diffraction and compared to reference charts.

4.5.2. Scanning electron microscope (SEM)

After the sintering process, the microstructures of the used specimens were photographed using a Scan Electron Microscope. The SEM test was used to determine the chemical composition and topography of the sample. The specimen is imaged using a high-pack of electrons; this test was carried out at the University of Karabuk in Turkey using an SEM (Carl Zeiss Ultra Plus Gemini FESEM), as shown in Figure 4.5.

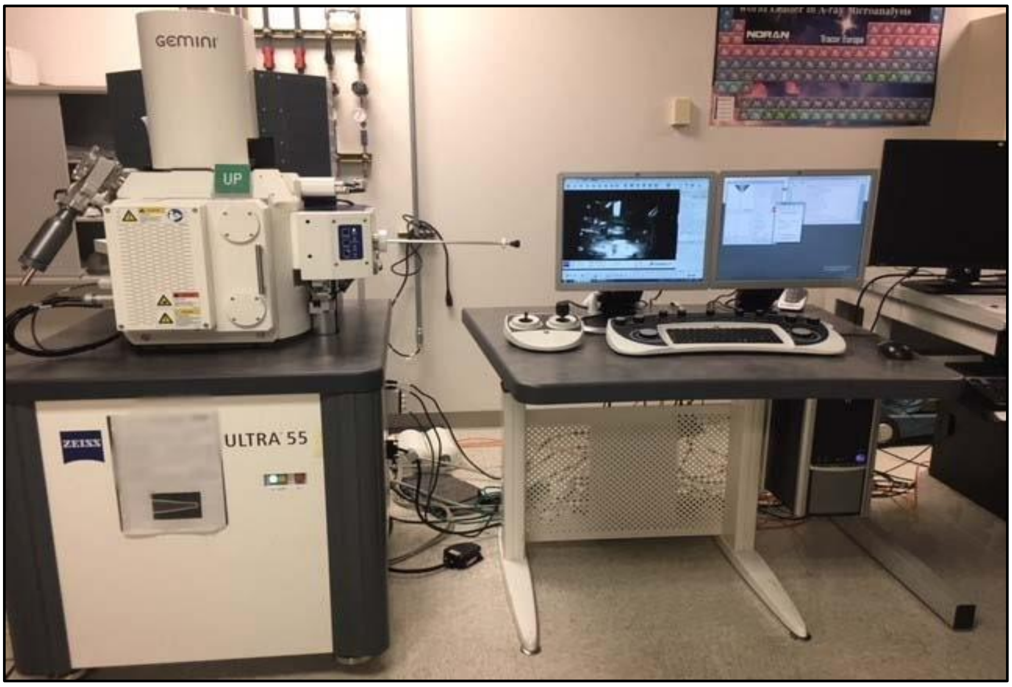


Figure 4.5. Scanning Electron Microscopy.

4.5.3 Energy Dispersive Spectroscopy

The analytical technique used for the chemical and elemental analysis of samples was using Energy-dispersive spectroscopy (EDS). The EDS device was coupled with SEM, and the inspection is shown in Figure 4.5.

4.6. PHYSICAL TESTS

Sintered samples may have their porosity estimated using the standards set out in ASTM B327 [97].

1-The specimen was dried up to 100 °C for 5hrs under vacuum (10^{-4}) and then cooled to room temperature using a vacuum drying furnace. The weight of the dry specimen is measured as mass A.

2- The specimen is brought to room temperature before being immersed in the oil for a period of thirty minutes. During this time, an appropriate vacuum pump is used to lower the pressure exerted on the submerged specimen.

3- After the oil immersion operation, the weight in the air is denoted by the mass symbol "B."

4- The specimen's weight while immersed in water is denoted by "Mass F.

5- In conclusion, it is possible to compute the porosity using the following equation, which is as follows:

$$p = \left[\frac{B-A}{(B-F)*D^{O}} * 100\right] * D_{W} \text{........(4.1)}$$

$$\rho = \left[\frac{A}{B-D}\right] * D_{W} \text{ .... (4.2)}$$

Where:

D_{W} – The density of water = $0.9956\ \frac{g}{cm^3}$

D^{O}- The density of oil= $0.634\ \frac{g}{cm^3}$

4.7 HARDNESS

The (Qness Q250M) was used to measure the macro hardness (Brinell) of the Ti-18Nb-xCu alloys by holding a 62.5 kg load on a 2.5 mm steel ball for 10 seconds. With a 1kg load and 15s dwell time, the microhardness (Vickers) was also measured with (QNESS Q10 A+). The average hardness was calculated using at least five measurements. The hardness of salt-added samples was also tested. The hardness devices are depicted in Figure 4.6.

Figure 4.6. QNESS Q250M Macro hardness tester.

4.8 DRY SLIDING WEAR TEST

At room temperature, the tribological characteristics of all produced specimens were examined using a UMT-2 tribometer. The gadget may be found at Karabuk University in Turkey. The kinematic form is a reciprocating linear motion for the micro-tester (ball-on-disk). A polished bearing steel sphere with a diameter of 10 mm and a roughness of 0.02 m was used to make the balls. With a constant sliding velocity of 1 mm/s and a constant load of 10 N. Figure 4.7 depicts an enlarged contact diagram of the frictional pair of the UMT-2 tribometer. The test cycles for each sample were 12500, at a frequency of 3 Hz and a stroke of 4mm. The wear recordings on the disc were done directly after the experiment.

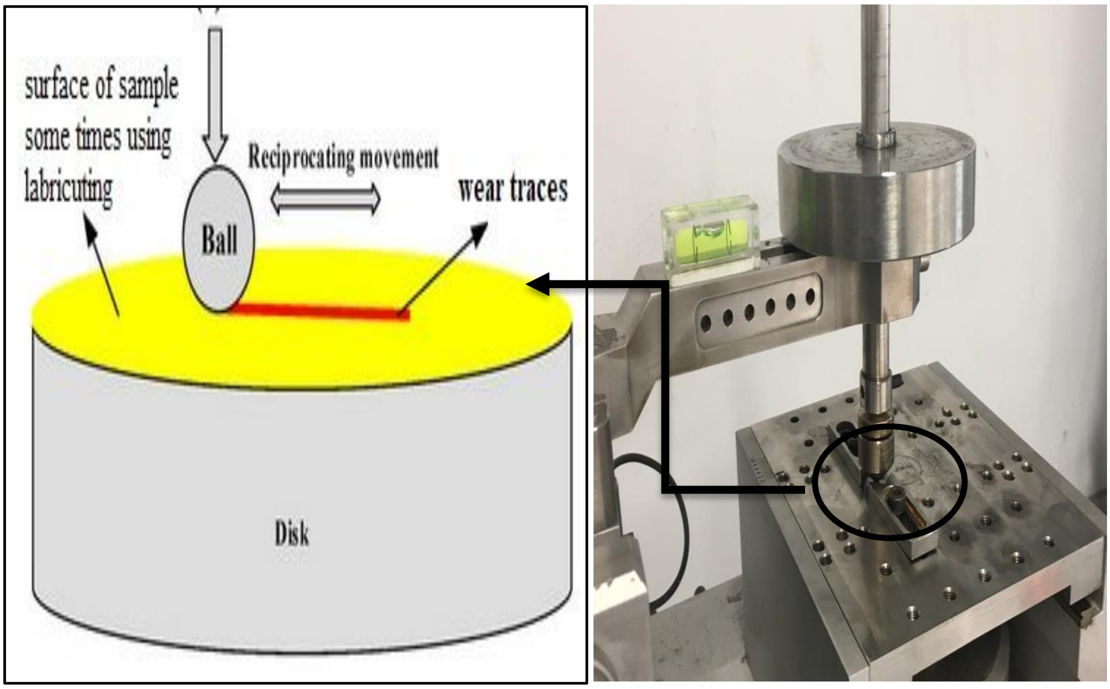


Figure 4.7 Ball-on-disc method.

Before starting the test, the specimen is weighed using a sensitive balance (0.0001) g. After the sliding distance, the specimen test was weighted, and the weight loss was determined.

4.9. COMPRESSION TESTS

An electromechanical machine, Zwick/Roell Z600, was used, with a maximum capacity of 100 kN. The test consisted of compressing the sample to the maximum stroke of the machine and establishing the strain rate as a fixed process parameter. The maximum stroke was limited until reaching a distance close to the machine base, the equivalent of 5 mm, for safety reasons. The uniaxial compression test was performed at room temperature, with a strain rate of 0.01 mm/s. During the test, data on applied force and compression displacement are generated. Knowing the characteristics of the sample, it is possible to calculate the stress (Equation 4.6), which is defined as the quotient between the applied force and the sectional area of the material.

$$\text{compressive strength (MPa)} = \frac{\text{Max force (N)}}{\text{cross section area (mm}^2\text{)}} \quad \text{.....(4.6)}$$

On the other hand, the specific strain (Equation 4.7) is defined as the relationship between the change in length and the initial length. It is also worth mentioning that the elastic modulus was calculated according to ASTM E9-2000.

$$\text{strain} = (Lf - Li)/Li * 100$$

Where: ε= specific strain (%)

L_f= final length (mm)

L_i= initial length (mm)

Biomedical implant materials are generally designed to deform elastically while being used. For this reason, the amount of energy (resilience) the materials can absorb during the elastic deformation stage is significant. Modulus of resilience (U_r), defined as the area of elastic deformation zone in the stress-strain graph, can be calculated with the following formula [98];

$$U_r = \sigma_y^2/2E \qquad \text{................(4.8)}$$

Where :

E: is the elastic modulus in the formula,

σ_y: is the yield strength.

PART 5

RESULTS AND DISCUSSION

5.1 INTRODUCTION

This part records all results of the physical and mechanical tests carried out for fabricated alloys (Ti-18Nb-xCu) will be viewed by XRD analysis, and the exam of surface morphology will be scanned by SEM/EDS analysis. These results are discussed to determine the best value for the effecting parameters on the responses of the prepared alloy samples. Also, the chapters include the results of the tests on the optimal alloy sample.

5.2. CHARACTERIZATION OF THE TI-18Nb-XCu ALLOYS

5.2.1. Density and Porosity

Table 5.1 provides the chemical compositions of the produced alloys and their observed average densities, and computed porosities. A porosity of around 18% shows that the density of the alloy may be enhanced. By adding the Zr element to (Ti–13Nb–13Zr) alloy, a similar effect (i.e., increased density) may be seen after sintering at 1250 C for 4 hours and 360 MPa compression pressure [99]. Ti-16Nb-2Sn had a density of 96.30 % at the maximum sintering temperature evaluated (1550 ℃), and adding Sn to the alloy increased the density even at lower sintering temperatures [27].

Table 5.1. Compositions and densities of alloys.

Sample	Porosity (%)	Density (g/cm^3)
$Ti-18Nb$	18.58±0.929	4.01 ± 0.097
$Ti-18Nb-5Cu$	17.48±0.874	4.17 ± 0.067
$Ti-18Nb-7Cu$	17.51±0.875	4.22 ± 0.057
$Ti-18Nb-9Cu$	17.59±0.879	4.27 ± 0.072

On the other hand, compared to the reference material, porosity dropped upon the addition of Cu and then stayed essentially unchanged regardless of the quantity of Cu added. This may be because the melting point of titanium copper alloys is reduced when copper is added [100]. It is known that porosity, pore shape, pore size, and pore homogeneity strongly affect mechanical strength and biological functionality; therefore, any fabricated material must be close to the properties of natural bone. In orthopedics, metals satisfy all the challenging factors involved in implant applications.

5.2.2. XRD Analysis

The microstructure phases formed after Cu incorporation were analyzed using XRD to determine how the element contributed to their formation (Fig. 5.1). Both α-Ti and β-Ti are visible in the Ti-Nb alloy. However, the phase patterns of Nb and β-Ti are practically coincident (2 θ; 38.3, 55.3, 69.3, and 82.1); therefore, they could not be recognized and labeled using conventional XRD analysis because of the small number of phases present. The XRD examination for a Ti-18Nb alloy showed the appearance of the Ti_2Cu phase when Cu was added, and as more Cu was added, the peaks at 43.6 and 77.5 for the Ti_2Cu phase were more pronounced, as predicted by the JCPDS (standard card No. 14-0641) for this phase. However, all of the alloys with Cu added showed the presence of the same phases. In a Ti-Cu alloy with a Cu content of less than 40%, the binary phase diagram predicts the formation of just the Ti_2Cu phase [25]. The $Ti - Nb - Cu$ triple-phase diagram shows that the and Ti are formed when less than 5 $wt.\% \ Cu$ is added to the $Ti - 18 \ Nb$ alloy, that the Ti_2Cu phase is formed, and that Ti_2Cu precipitates expand as the Cu concentration is increased. As shown by this phase diagram, the structure basically consists of β-Ti and Ti_2Cu as Cu content rises. This proves that the concentration of Cu is favorable for forming the phase [25].

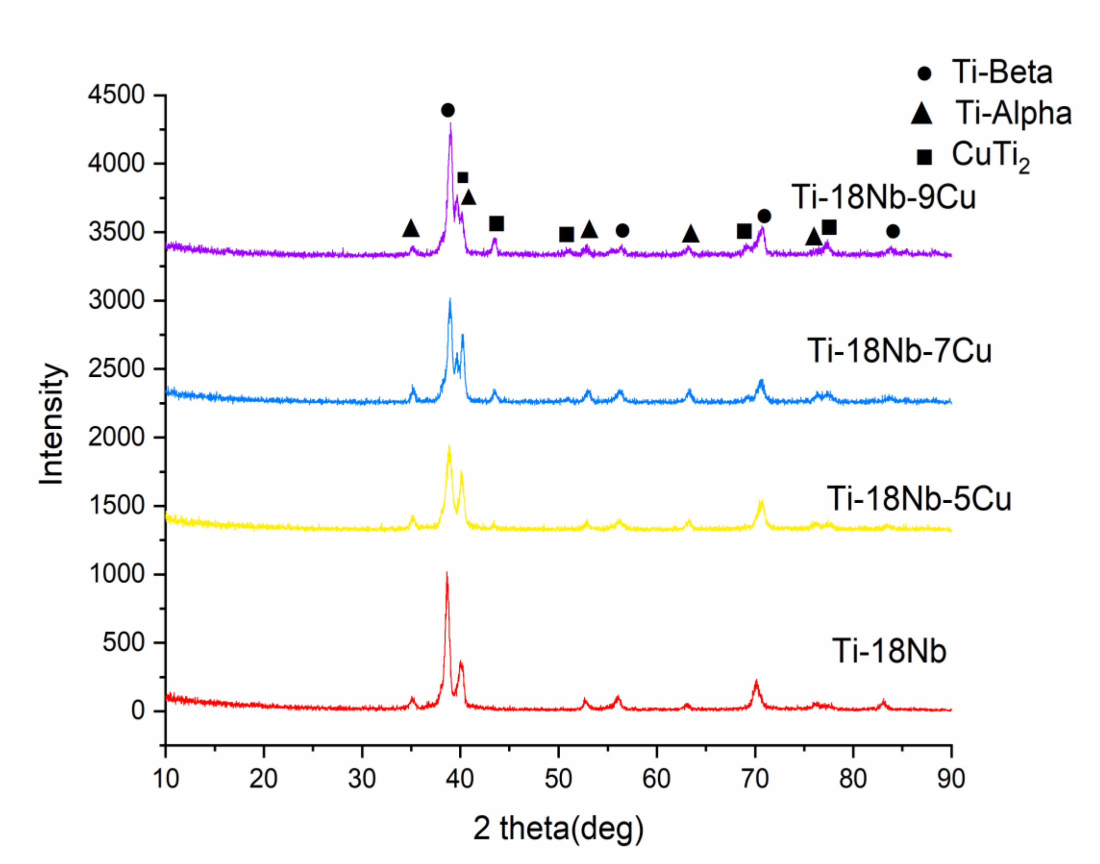


Figure 5.1. XRD analysis of prepared alloys.

5.2.3. SEM/EDS Analysis

Figure 5.2 illustrates the microstructure of Ti-18Nb alloy, which comprises α -Ti and β -Ti phases and a minor quantity of undissolved Nb. However, there are Nb-rich spots in the Ti-18Nb alloy. The white areas represent Nb regions that contain nearly no Ti, while the light gray regions at the phase's boundary contain (⅔wt%) Nb. Although white microstructure regions are uncommon, light gray microstructure regions are dispersed throughout. The lack of such Nb-rich patches in Cu-added alloys suggests that Cu addition promotes sintered state.

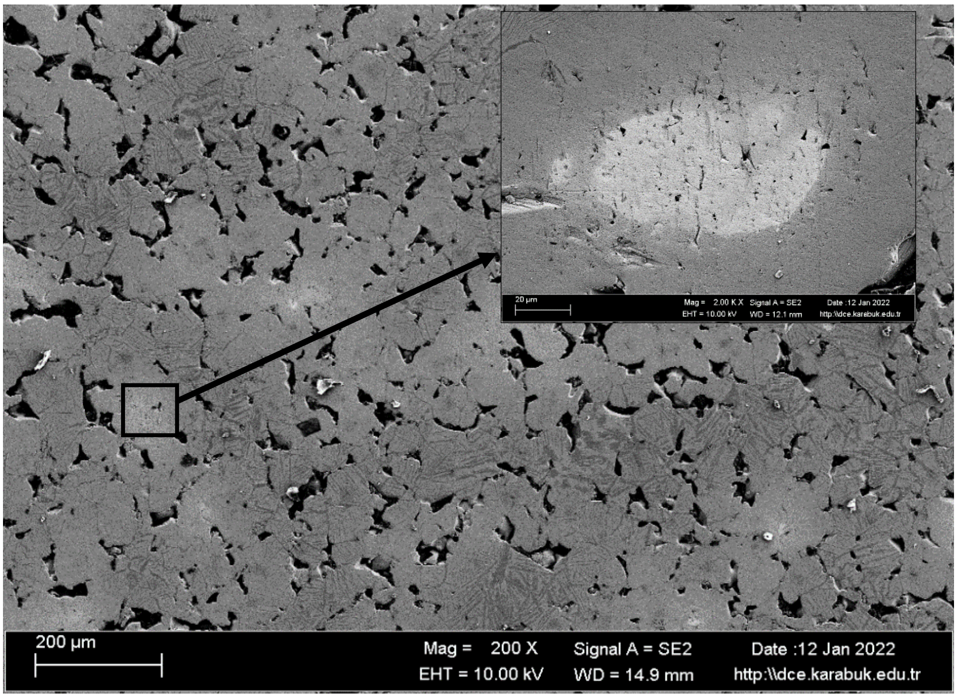


Figure 5.2. Microstructure of the Ti − 18Nb alloy.

At around 900 °C, the Nb particles begin to dissolve, initiating the formation of the β-Ti structure in the overall microstructure, the amount of which increases as the temperature rises [55]. It was shown that Nb-rich phases existed in both Ti-10Nb and Ti-15 Nb alloys up to 1100°C after they were sintered at temperatures ranging from 900°C to 1500°C. In addition, the shape of these Nb-rich phases was irregular after sintering at 900°C and spherical after sintering at 1100°C, as Martins et al. [103]. According to Zhao et al. [101], the sintering temperature of Ti-Nb alloys should be 1300°C on average for full homogeneity. Our research found that Cu addition aided homogenization and that 1150°C was adequate for Cu-added materials.

Cu-added alloys have a homogenous microstructure with dark and light-colored regions. The amount of Nb increases in the light-colored regions and decreases in the dark regions (Fig. 5.3 with line EDS). The light-colored regions where the amount of β- stabilizer Nb increases are called β-Ti, while the other dark-colored regions are called α-Ti. Slow cooling in the furnace after sintering led to the dissolution of the α-Ti phase and the creation of the β-phase or eutectoid. Microscopically, the main β-Ti phases appear as thick dark gray regions (Fig. 5.3). Very fine α-phase formation or martensitic transformation was not observed depending on the cooling rate.

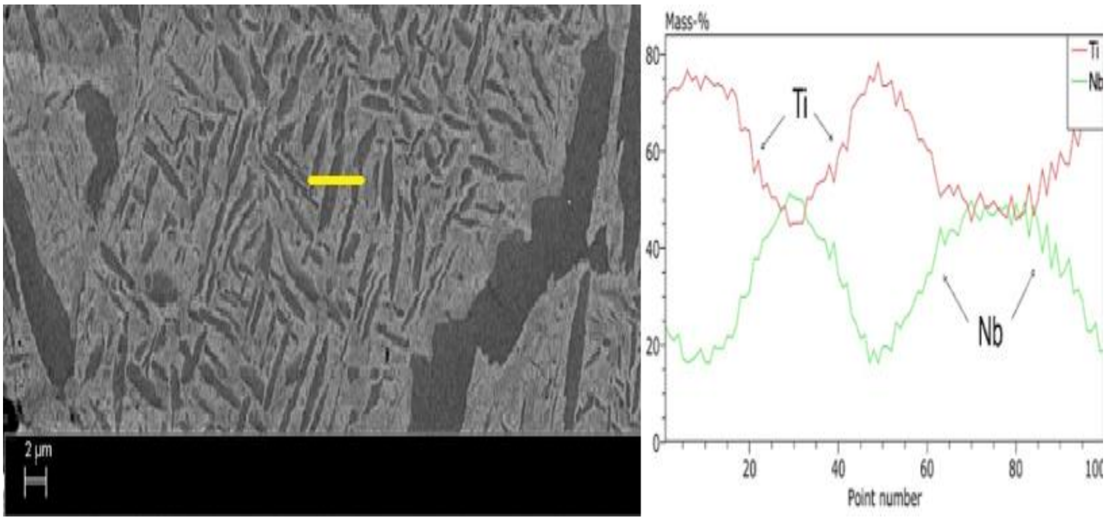
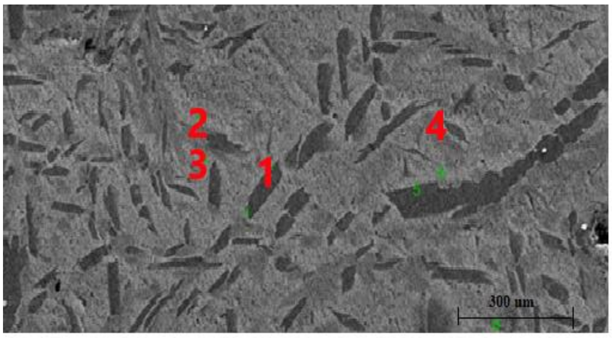


Figure 5.3. Microstructure of the $Ti - 18Nb - 7Cu$ alloy and line EDS analysis.

The microstructure of alloys containing Cu is generally comparable, although the 9 wt. % Cu alloy displays distinctively colored (ash gray) phases at the boundaries of the dark gray phases (α-Ti). The microstructure of the whole alloy is usually responsible for this creation (Fig. 5.4). It has been determined from point EDS analyses of the microstructure that the dark regions all correspond to the α-Ti phase, whereas analysis regions 4 and 8 are β-Ti. The Cu and Nb-rich sections of the α -Ti phase may be seen in the ash-gray areas 1, 3, and 7 generated in this microstructure, which stands in contrast to most alloys. Line EDS examination of the targeted area reveals that the concentration of Nb rises slowly in the gray ash created after α-Ti, whereas the concentration of Cu rises above β-Ti, a phenomenon not seen in the remainder of the β-Ti phase. In order to facilitate the creation of α-Ti, increasing the quantity of Cu caused Cu to diffuse into α -Ti with thermal activation energy and form a solid solution [102].



Mass percent (%)			
Spectrum	Ti	Cu	Nb
1	88.33	0.00	11.67
2	86.67	2.14	11.19
3	53.21	0.00	46.79
4	87.09	2.44	10.46

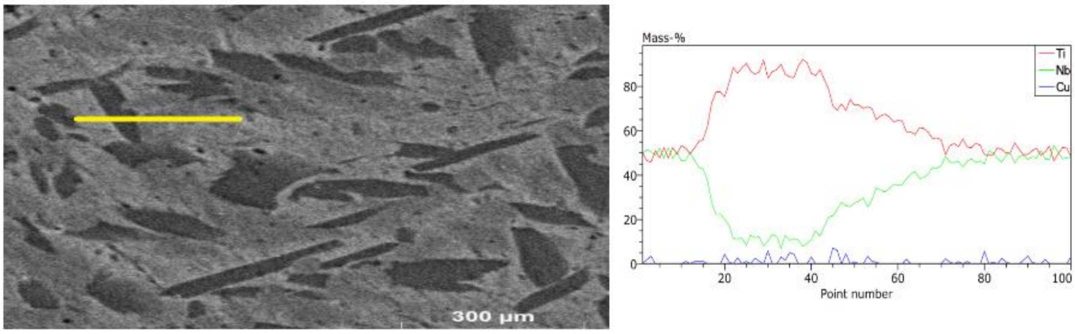


Figure 5.4. Microstructure of the Ti − 18Nb − 9Cu alloy and line EDS analysis.

It can be observed in Figure 5.5, which provides an overarching perspective of the microstructure of the produced alloys, that the off-white strip or lump substances are uniformly dispersed throughout the surface of the porous Ti_2Cu phase.

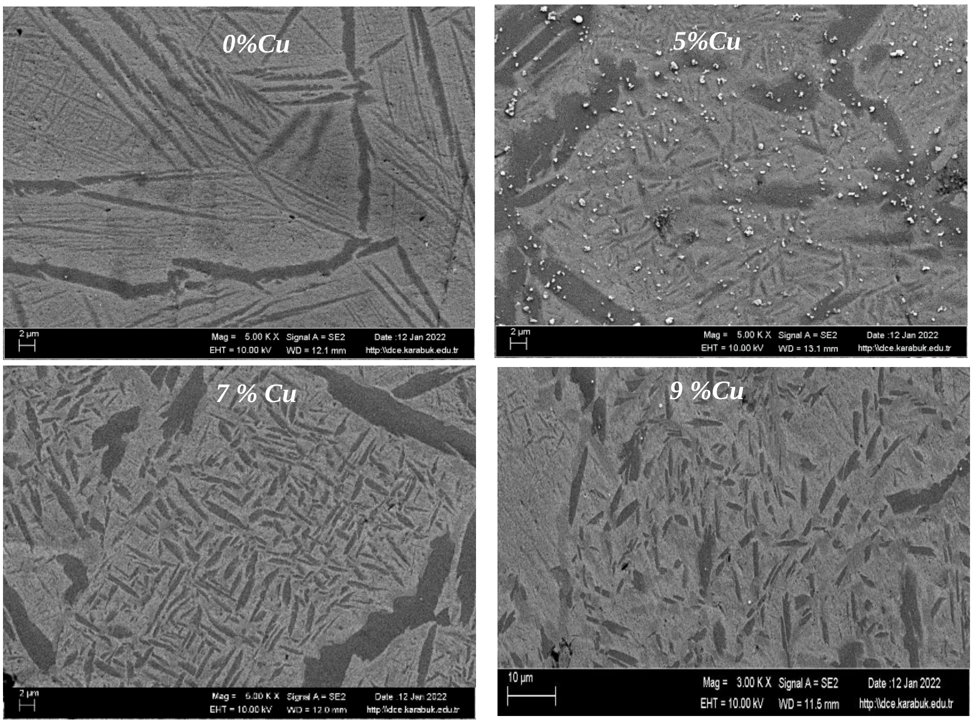


Figure 5.5 Microstructure of the Ti-18Nb-xCu alloys.

5.2.4. Compression test

The microstructure and mechanical properties of Ti-18Nb changed when Cu was added to it. The compression test for prepared alloys illustrated in Figure 5.6 demonstrates that specific mechanical properties may be calculated by applying varied loads to assess the change in mechanical characteristics. Figure 5.7 and Table 5.2 show the data. The calculated mean values were frequently within a 10% standard deviation range.

The data show that as more Cu was added, the yield strength of the Ti-18Nb alloy rose almost linearly. The compressive strength, however, increased slightly with 5 wt.% Cu then increased significantly with increasing Cu and then increased slightly with increasing Cu. The effect of adding copper to titanium at various rates (2, 5, 7, and 10 wt.%) was studied, and the findings revealed that the alloy composed of titanium and seven weight percent of copper had the maximum compressive strength [29]. Similarly, this study shows the compressive strength of the alloy with 7 wt.% Cu added significantly increased, but there was almost no increase in the increasing Cu addition. With increasing Cu addition, the alloy's elastic modulus (E) was studied; it was shown to rise marginally with a 5 wt.% Cu addition and decrease with increasing Cu addition. Yuan et al. [103] Cu was added to the Ti-13Nb-13Zr alloy at various rates (4, 7, 10, and 13 wt%), and the authors reported that the compressive and yield strengths rose with increasing Cu, but the modulus of elasticity declined and subsequently increased with increasing Cu. In the alloy with 7Cu additions, the lowest point in the modulus of elasticity was observed. The lowest modulus of elasticity was found in the $\mathrm{Ti}-18\mathrm{Nb}-7\mathrm{Cu}$ alloy, and a comparable shift was seen with the inclusion of Cu in the alloy in a similar phase (α and β).

The modulus of elasticity of the bulk (arc melted) $\mathrm{Ti}-15\mathrm{Nb}$ alloy is 77 GPa, and that of $\mathrm{Ti}-7\mathrm{Cu}$ is 108GPa [29, 30]. It is well known in this context that production parameters and pore size substantially impact defining modulus of elasticity. On the other hand, it has been discovered that cancellous bone has a modulus of elasticity of just 3 GPa, but compact human bone has a modulus of elasticity of 12-17 GPa [104, 105]. Consequently, it has been seen that the produced alloys are generally suitable in terms of modulus of elasticity, which affects stress shielding.

As predicted by the formula, a high resilience value could benefit bio-applications where yield strength and elastic modulus are both high.

$Ti - 18Nb$ alloy, with its lowest Cu concentration, was found to have the lowest resilience among the manufactured materials. The range for this value is given as $1 - 5\ MJ.m^{-3}$ in many Ti alloys [106], was determined as 3.7 in TAV alloy[107]. The Ti-10Mo-1.25Si-10Zr alloy, which is in the β-Ti phase, increases up to $22.56\ MJ.m^{-3}$ [108].

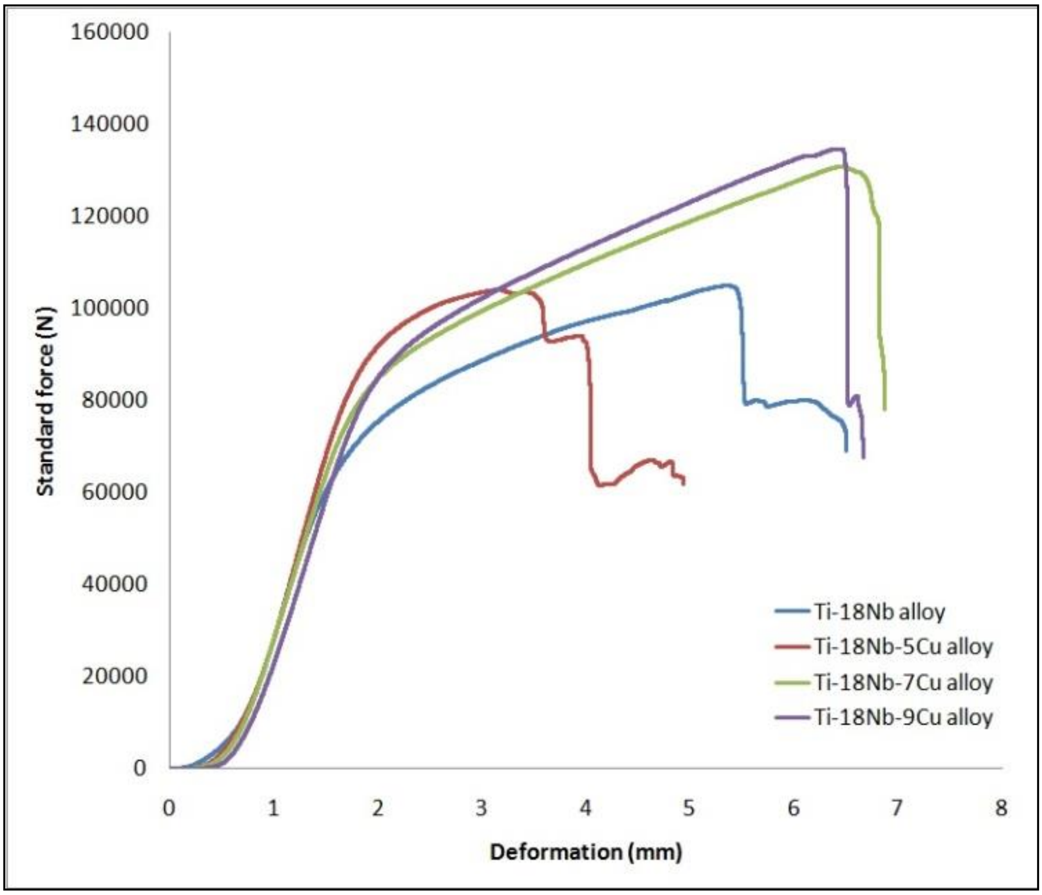


Figure 5.6 Stress-strain curve for Ti-18Nb-xCu alloys.

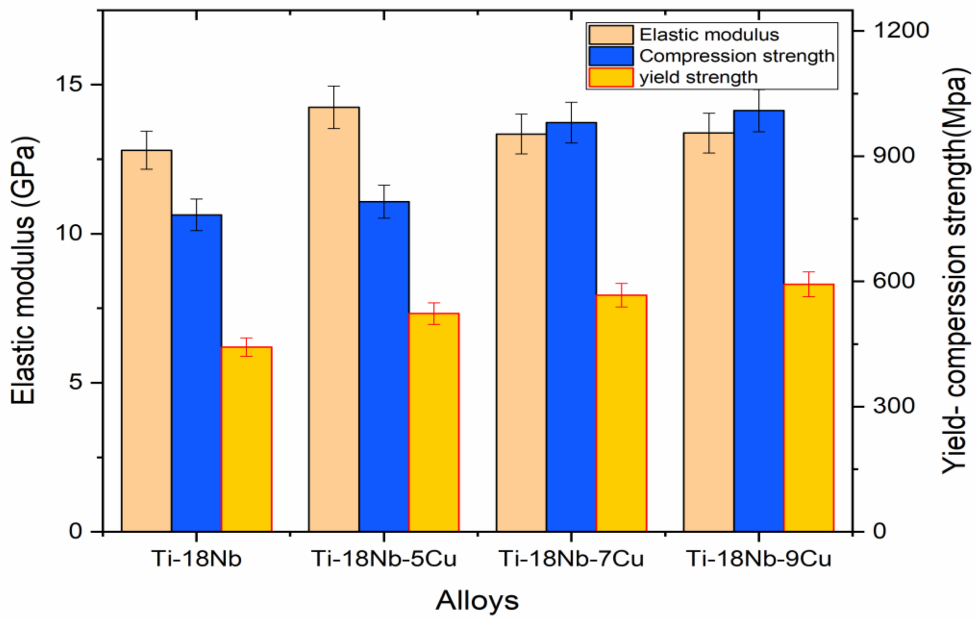


Figure 5.7 Mechanical properties data for tested alloys.

Table 5.2. Average mechanical values of the samples.

Sample	Mechanical Properties			
	E (GPa)	σ_{max} (MPa)	σ_y (MPa)	U_r (MJ/m^3)
$Ti-18Nb$	12.800±0.640	759.61±37.9	442.68±22.1	7.65±0.38
$Ti-18Nb-5Cu$	14.244±0.712	791.10±39.5	522.87±26.1	9.60±0.48
$Ti-18Nb-7Cu$	13.343±0.667	980.49±49.0	566.90±28.3	12.04±0.60
$Ti-18Nb-9Cu$	13.377±0.668	1009.20±50.4	593.08±29.6	13.15±0.65

5.2.5 Hardness test

The alloy with 7 wt.% Cu addition had the maximum hardness value determined, and afterward, the hardness value stayed the same or slightly declined as the Cu content increased. The precipitation of the Ti_2Cu phase and the solid solution strengthening that may occur in the α-Ti phase is responsible for this hardening [108]. The formation of similar phases in $Ti-18Nb-xCu$ alloys shows that the increase in hardness may be due to a similar reason. A similar trend was observed between the micro and macro hardness measurements, but the macro hardness was slightly lower due to manufacturing defects, as shown in Figure 5.8 and Table 5.3.

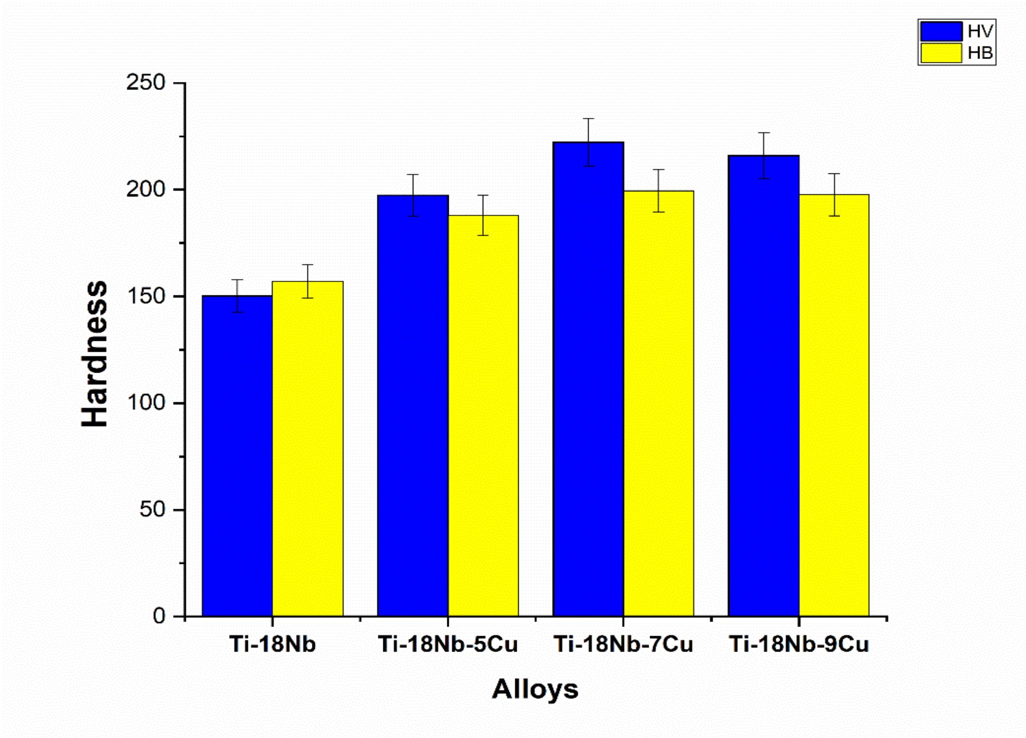


Figure 5.8 Hardness values for prepared alloys.

Table 5.3. Average hardness values of the samples.

Sample	Hardness	
	HV	HB
$Ti-18Nb$	150.25±7.5	110.0±5.5
$Ti-18Nb-5Cu$	197.33±9.8	131.67±6.58
$Ti-18Nb-7Cu$	222.20±11.1	139.60±6.98
$Ti-18Nb-9Cu$	216.0±10.8	138.40±6.92

5.3 EFFECT OF SALT ON PROPERTIES OF Ti-18Nb-9Cu ALLOY

Because of the importance of the amount of energy (resilience) that the materials can absorb during the elastic deformation stage is essential for bioapplication, $\mathrm{Ti}-18\mathrm{Nb}-9\mathrm{Cu}$ alloy has been selected (where it had the highest (U_r)) to study the effect of salt added to improve the properties to be closed to natural human bone. Four weight percent of salt were added, including (30, 40, 50, and 60 vol.%).

5.3.1 Characterization of the Ti-18Nb-9Cu with salt

The salt addition did not the formed phases and structure of prepared alloys because the salt will disappear after the sintering process, as shown in XRD patterns and SEM images in Fissures 5.9 and 5.10, respectively.

The space holder technique is a promising approach to creating metallic biomedical scaffolds due to its ability to provide a broad range of porosity levels and adjustable pore shape [109, 110]. Since sodium chloride (Ammonium carbonate (NH_4HCO_3)) is very cheap, highly soluble in water, relatively non-toxic, commercially accessible, and easily removed using solvent-debinding methods, it is often utilized as the space-holding material. Furthermore, in vivo performance is unaffected by Ammonium carbonate (NH_4HCO_3) residues [111]. However, it must be processed first to get rid of the crystal water before it can be used, or else it will detonate and disintegrate when heated to a certain point. When it crumbles, ammonium carbonate (NH4HCO3) fills up the prepared mold's cavities, forcing it to deform. The Ammonium carbonate (NH_4HCO_3) particles are dried out and stored in a desiccator until needed.

Some workers successfully produced porous titanium by plasma treatment [112], but eliminating the post-process is crucial in reducing the total process cost. Titanium with a porous structure may be manufactured using a space holder approach and powder injection molding.

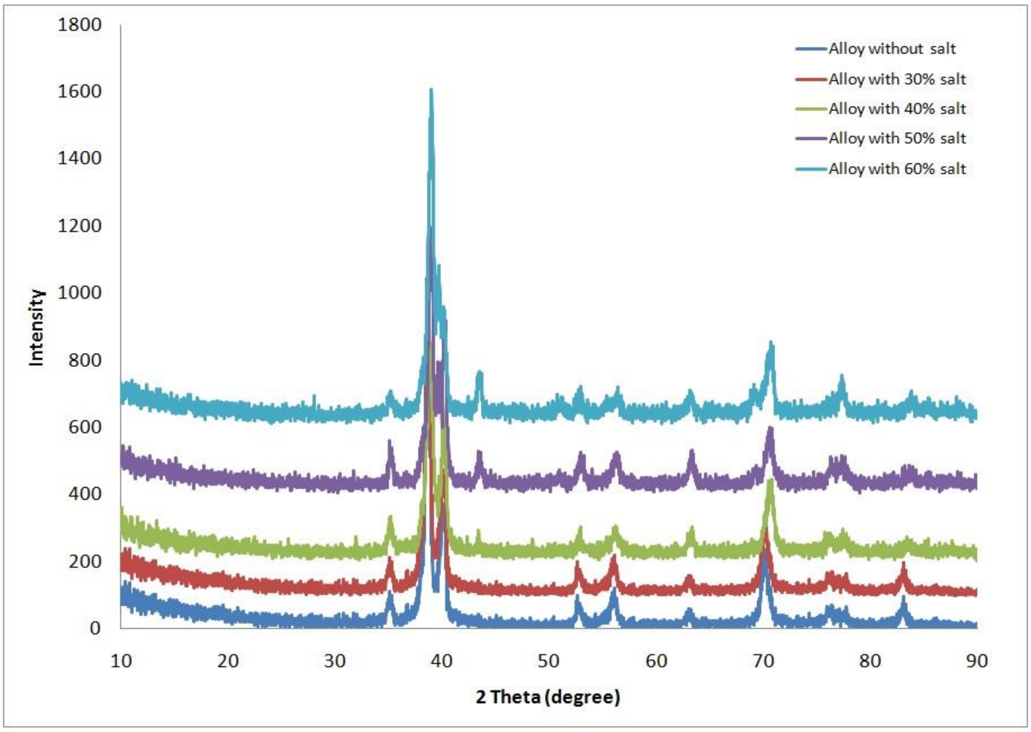


Figure 5.9 XRD patterns for prepared alloys with different percentages of salt.

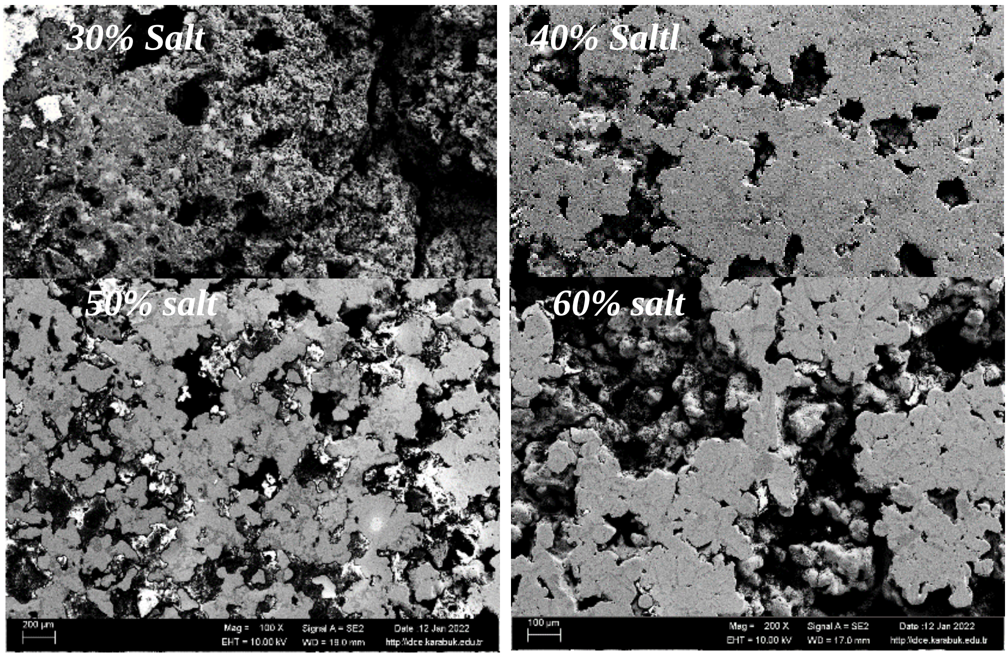


Figure 5.10 SEM images of Ti-18Nb-9Cu alloy with different percent of salt.

5.3.2 Density and porosity

When ammonium carbonate (NH_4HCO_3) was added, holes developed, causing the material's density to drop (as shown in Table 5.4). However, this fall in density was not uniform; it decreased by different amounts for different salt concentrations. The percentage of Ammonium carbonate injected affects porosity, with 60% Ammonium carbonate producing the most porous material. Porosity created by a reduction in particle density promotes rapid cell development after implantation. In this case, the porosity of the rectangular pores was similar to that of the Ammonium carbonate (NH_4HCO_3) space holder material, demonstrating that pore shapes are influenced by the shape and size of the particles of the powder components used in the space holder.

Table 5.4. Densities of Ti-18Nb-9Cu alloy after adding salt.

salt Vol %	**Density (g/cm^3)**	**Porosity (%)**
0	4.27 ± 0.072	9.08
30	3.62± 0.072	31.26
40	3.63± 0.072	37.98
50	4.08± 0.072	51.06
60	3.75± 0.072	60.66

5.3.3 Mechanical properties

The addition of ammonium carbonate affected the mechanical properties, as shown by measuring the compression and hardness. Fig. 5.11 indicates the compression curves of $\mathrm{Ti}-18\mathrm{Nb}-9\mathrm{Cu}$ alloy after adding ammonium carbonate with four percent (30, 40, 50, and 60 vol.%), which are different from that recorded in the absence of ammonium carbonate.

The data concluded from the compression test are listed in Table 5.5, and Figure 5.12, which show that the compressive strength gradually decreases from 167.795 to 42.482 MPa when the salt content increases to 60 vol.%, and this behavior is expected due to the increase in the porosity content because the porosity is positively related to the material's resistance to compression; as can be seen in Figure 5.12, Young's modulus behavior of samples obtained at varying salt concentrations indicates that the presence of salt decreases compressive strength. Many different porosities and Young's moduli are shown in this graphic, all of which correlate to different salt concentrations. This graph illustrates how Young's modulus decreases as porosity increases. Verifying the negative correlation between Young's modulus and Ammonium carbonate (NH_4HCO_3) concentration is of more importance. The characteristics of human cancellous bone are similar to these. In its hydrated, natural condition, the Cancellous bone has a strength of 2-6 MPa and Young's modulus of 0.1-0.3 GPa [113]. Cancellous bone has a much lower strength and Young's modulus than cortical bone (110-150MPa and 18-22 GPa, respectively) due to its increased porosity and pore size. The relationship between the mechanical properties and the percent of salt is shown in Figure 5.12.

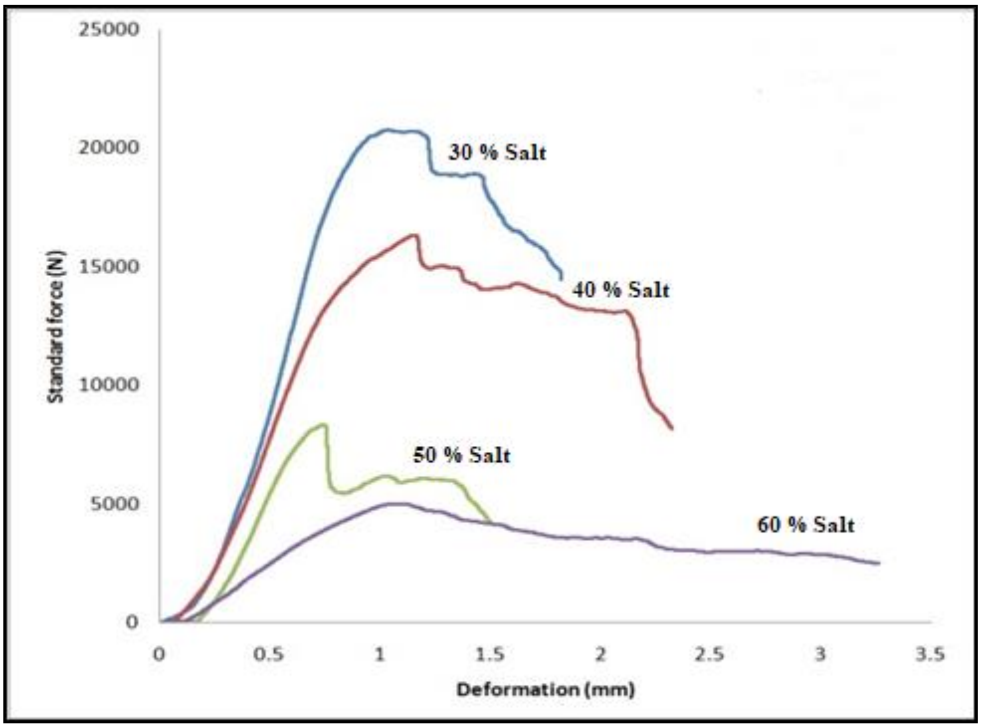


Figure 5.11 Compression curve for $Ti-18Nb-9Cu$ alloy after salt addition.

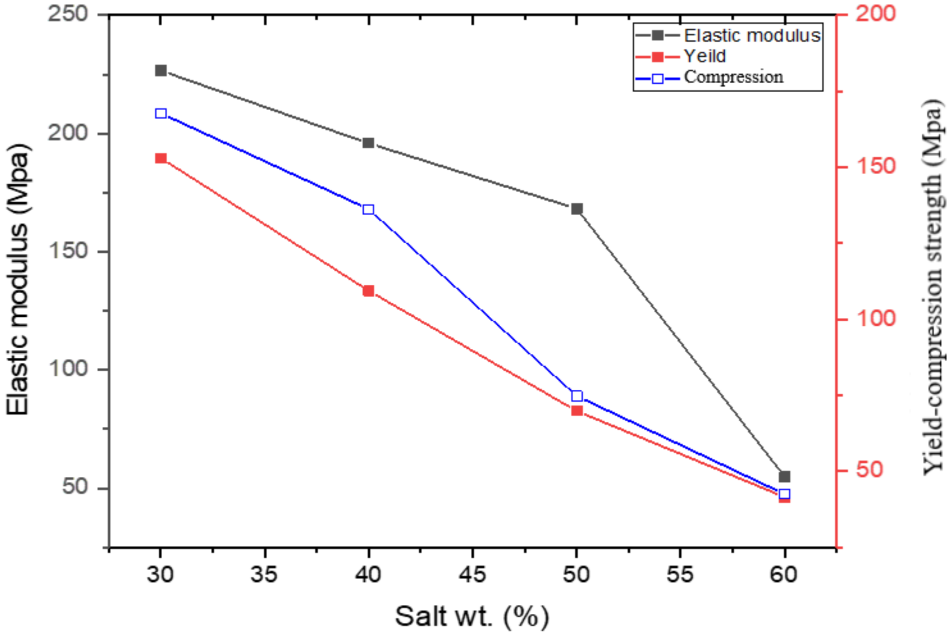


Figure 5.12 Mechanical properties of Ti − 18Nb − 9Cu alloy after salt addition.

Table 5.5. Average mechanical values of the samples.

Salt Vol%	**Mechanical Properties (MPa)**		
	E	σ_{max}	σ_y
30	226.562	167.795	153.071
40	195.883	136.188	109.382
50	168.192	74.793	69.815
60	54.776	42.484	41.541

5.3.4 Hardness

Brinell hardness measurements were conducted for Ti-18Nb-9Cu alloy specimens with varying salt concentrations, and the results are shown in Table 5.6.

For the Ti-18Nb-9Cu systems, hardness values are found to be a function of salt content. Solid solution hardening of alloying elements combined with a linear behavior kept the hardness of the alloys above the value of Ti-18Nb-9Cu alloy (138.40) [5, 114].

The Brinel hardness (HB) decreased from (53.5 to 27.3 HB) with increasing factors content from 30 wt. % to 60 wt. % salt.

Mechanical characteristics of manufactured Ti-18Nb-9Cu with varying salt concentrations were studied by measuring hardness to determine the impact of pores on these parameters. The hardness of the manufactured material is shown in table 5.4 as a function of porosity for the deposition circumstances of this investigation. Consensus with Karthikeyan et al. [115], according to the findings, the material's hardness decreases as its porosity percentage rises. For instance, going from 29.73 to 48.09 percent porosity increased the hardness from 53.5 to 27.3 HB, a change of 61 percent. Density and lack of porosity are positively correlated with microhardness.

Table 5.6. Average hardness values of the samples.

Salt Vol%	**Hardness HB**
30	53.5±2.67
40	48.7±2.43
50	37.0±1.85
60	27.3±1.36

5.3.5 Wear test

Specimens with (13) mm diameter were subjected to dry wear test under constant loads 10 N at constant sliding speeds of 1 mm · sec^{-1}. The surface roughness of the test samples was measured. The determined average roughness value (Ra) is given in table 5.7. In addition, the surface roughness change is given in Figure 5.13. As can be seen from these results, the surface roughness increased as the salt content increased**.**

Table 5.7. Surface roughness values of the samples.

Salt Vol%	Surface roughness µm
30	0.969
40	1.522
50	1.901
60	1.982

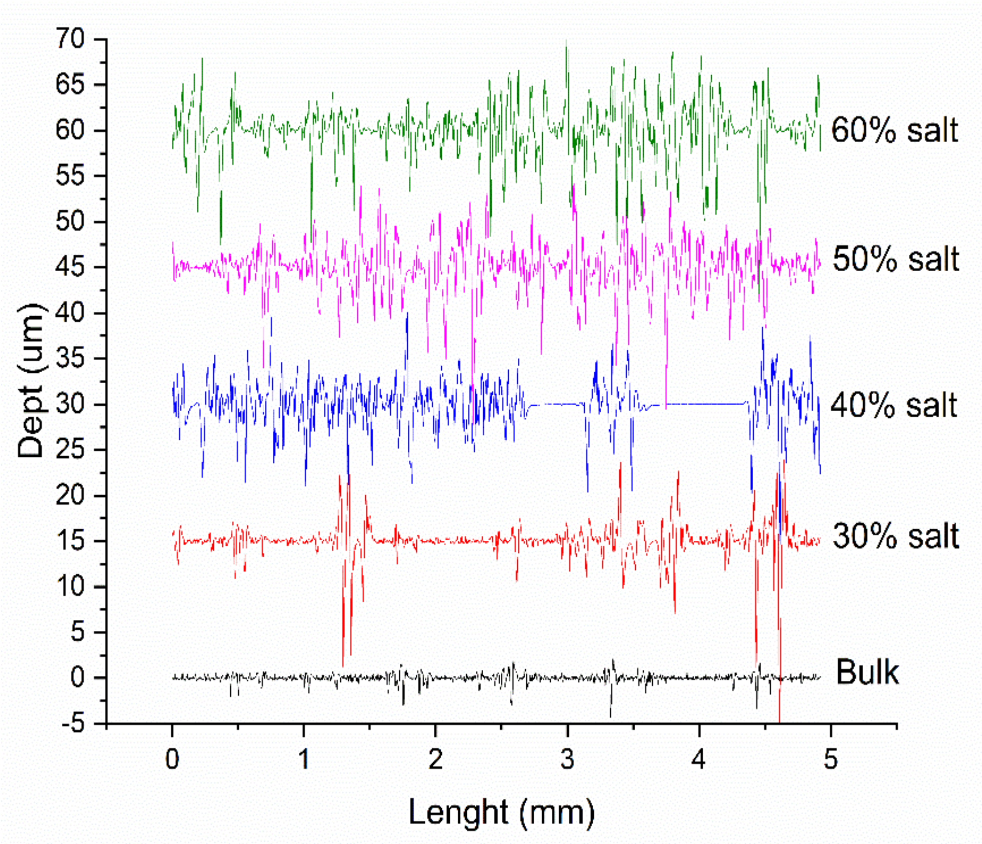


Figure 5.13. The change of surface roughness of the samples.

The variation of the friction coefficient for each sample during the wear test is given in figure 5.14. According to these data, the coefficient of friction in the bulk material was high, and the wear loss was higher than expected. On the other hand, in porous materials, a generally low coefficient of friction (average 0.2) was determined. This probably resulted in less wear loss. On the other hand, increasing porosity decreased the material strength, and fractures were observed.

Table 5.8 show the variation of volume loss weight of Ti-18Nb-9Cu without and with (0, 30, 40, 50, and 60 Vol.% of salt) under constant load 10 N. From this table, it is clear that the worn area increased with increasing salt concentration.

Table 5.8. The weight loss and worn area of the samples

Salt Vol.%	**weight loss mg**	**worn area mm^3**
Bulk	0.062	1.932
30	0.0004	0.287
40	0.002	0.357
50	0.003	2.184
60	0.003	2.324

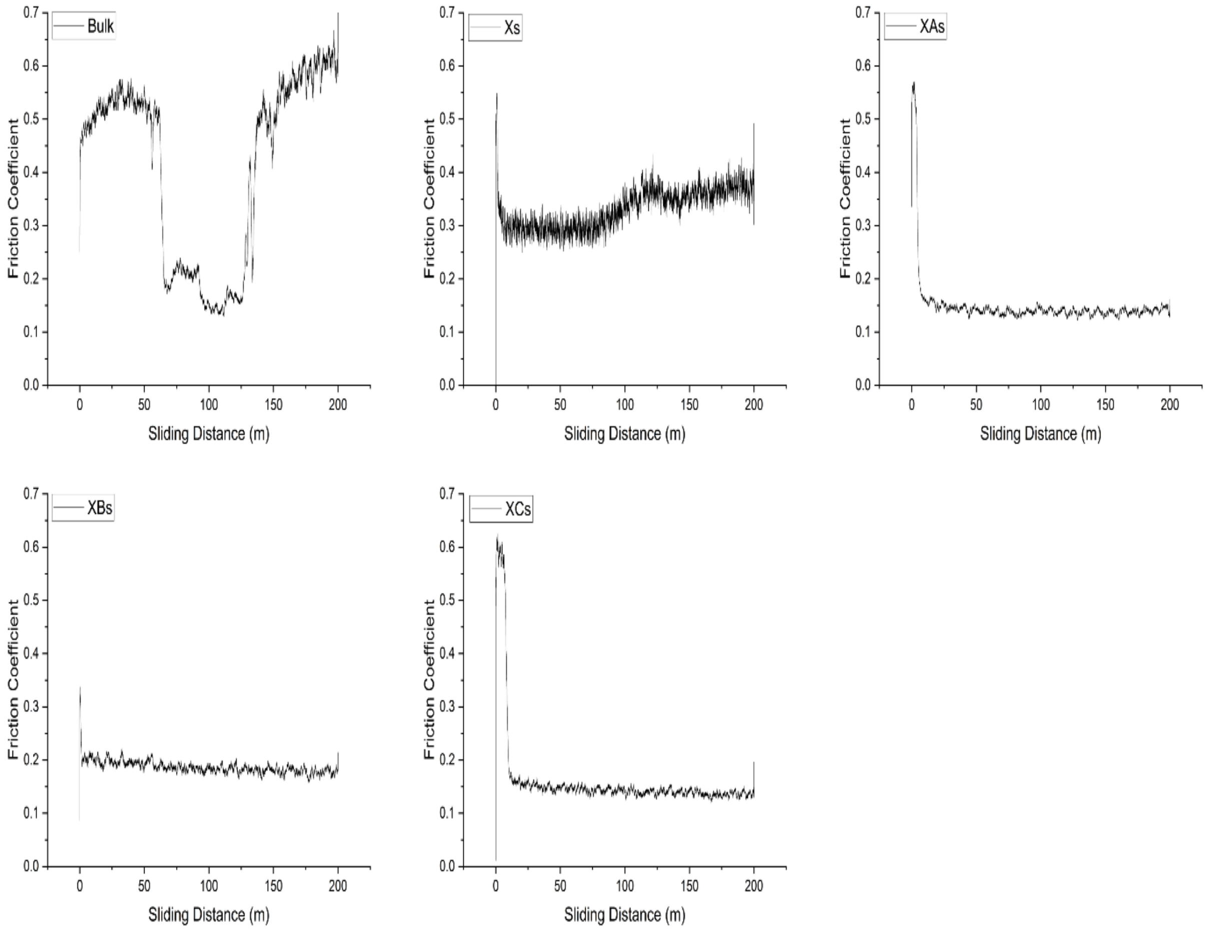
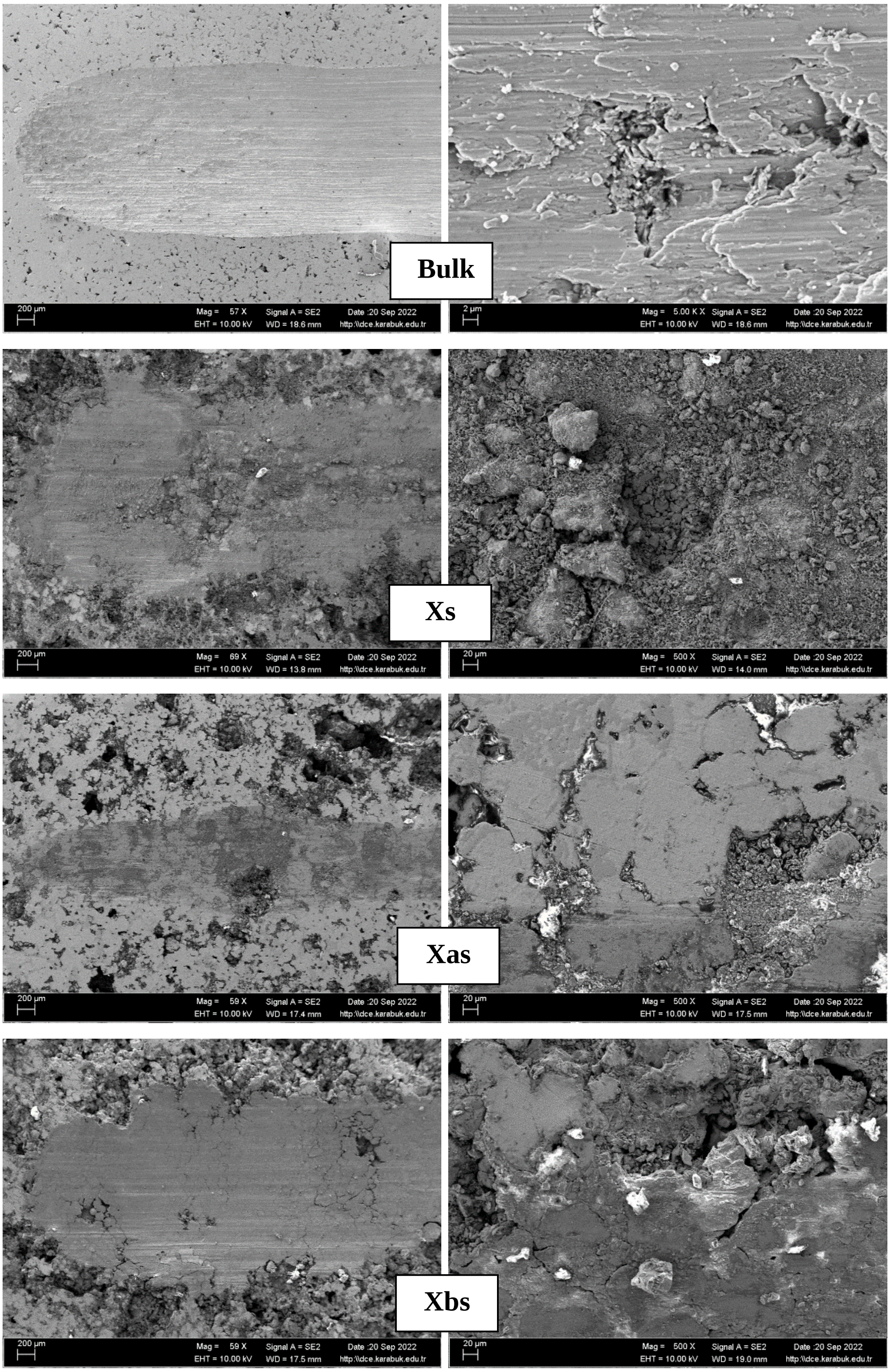


Figure 5.14. The friction coefficient of the prepared alloy with salt.

To study the surface of the specimens after the volume loss, many images of the surface were taken by SEM, as shown in the following Figure.



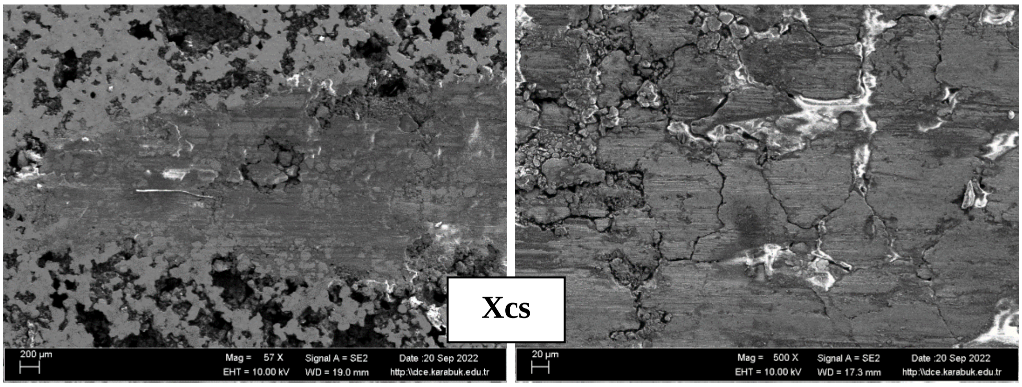


Figure 5.14. Microstructure of the prepared alloy with salt after wear test under10 N load.

Figure 5.14 shows the microstructure of the worn surface of the examined specimens, demonstrating the morphology of the worn surfaces of all the alloys, proving that wear occurs on all of them. Where the solid abrasive ball has penetrated the surface of the specimen, leaving behind wear regions and plastic deformation seen on the wear tracks. The time it takes, the force used, and the tested object's hardness affects the wear depth.

PART 6

CONCLUSIONS AND RECOMMENDATION

6.1 CONCLUSIONS

In this work, the transformations of phases and mechanical properties of alloys of the Ti-18Nb, Ti-18Nb-XCu, and porous Ti-18Nb-XCu system were investigated, and the results obtained allow us to state the following conclusions:

i. Ti-18Nb and Ti-18Nb-XCu alloy was prepared with different addition ratios of Copper by powder metallurgy (PM) method. XRD results showed that the sintering temperature at 1150°C for 5 hours is sufficient to transform the used elements into an alloy structure.

ii. Analysis by XRD shows that the prepared alloys have α and β phases structure with $CuTi_2$ compound appearing; in addition, a proportion of Cu is present in the Ti-18Nb-9Cu alloy.

iii. The density increases with the increase of the copper content. It was in the range (of 4.01-4.27 g/cm^3), while the porosity decreased when copper content rose, whose values were within (18-58-17.59 %).

iv. The hardness of the Ti-18Nb alloy increased with increasing Cu addition, and the highest hardness value was measured as 222 HV in the Ti-18Nb-7Cu alloy, but the hardness decreased a little with the addition of 9 wt.% Cu.

v. Compression and yield strengths of Ti-18Nb alloy increased with increasing Cu addition.

vi. The modulus of elasticity slightly increased with 5 wt.% Cu and then decreased with the increasing amount of Cu, The resilience values of the alloys were enhanced with the addition of Cu and the increasing amount of Cu.

vii. The addition of ammonium carbonate (NH_4HCO_3) as a spacer holder led to an increase in the porosity from 17.59 to 48.09 % of the Ti-18Nb-9Cu

viii. The mechanical properties decrease with an increase in the salt concentrations from 30 to 60 %

As a result, it is thought that Ti-18Nb-9Cu alloy may be a potential implant alloy in terms of its mechanical properties, with higher yield strengths than pure Ti alloy, higher resilience than TAV alloy, and low modulus of elasticity.

6.2 Recommendations

The results obtained in the course of this investigation allow us to suggest the continuation of studies through the following lines of complementary research:

i. After a titanium alloy has been shaped, more processing steps are required to get the desired results. Quenching and heat treatment are two easy procedures that may be used to achieve this.
ii. Evaluate the effect of shape memory and corrosion fatigue of the Ti-18Nb-XCu alloy.
iii. Perform in vitro tests to assess the genotoxicity of the studied alloy;
iv. study the fatigue test of the investigated alloy.
v. Characterization of the biocompatibility for the prepared alloy

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