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Effets de la porosité sur les propriétés élastiques des couches et alliages semi-conducteurs

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وَفِي الْأَرْضِ آيَاتٌ لِلْمُوقِنِينَ ۞ وَفِي أَنْفُسِكُمْ أَفَلَا تُبْصِرُونَ ۞

وَفِي السَّمَاءِ رِزْقُكُمْ وَمَا تُوعَدُونَ ۞ فَوَرَبِّ السَّمَاءِ وَالْأَرْضِ إِنَّهُ

لَحَقٌّ مِثْلَ مَا أَنَّكُمْ تَنْطِقُونَ ۞. [الذاريات: 20-23]

DEDICATION

To the pure soul of my Father who is my destiny ....

I pray ALLAH to keep the souls and body of my mother who is the light of my life ....

To my wife who stands with me all the time and encourage me in my life And my educational and scientific trip she is my heart ......

To all my sons SAAD and KHALID are Eyes that I see.........

To all my Brothers and Sisters Who are my wings ......

To all my Family.......

To all my Friends.......

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دراسة التأثير المسامي على الخواص المرنة لطبقات وسبائك أنصاف النواقل.

من طرف: يحي الصياد

المُلخص

درسنا في هذا البحث سبائك Ti-6Al-4V التي يمكن استعمالها في تعويض العظام البشرية. تتميز هذه السبائك ببنية مسامية. ولهذا اهتممنا بدراسة تأثير المسامية على الخواص الميكانيكية (معامل يونغ، القص، الحجم) والوسائط الصوتية (معامل الإنعكاس، الإمضاء الصوتي، السرعات الطولية، والعرضية ورايلي والممانعات الصوتية). تم حساب تأثير المسامية لكل الوسائط التي وجد أنها تتناقص أسيا. كما تمكنا من إيجاد العلاقات المناسبة:

للثوابت المرنة: $M = A + \beta e^{-c P (\%)}$

والسرع الصوتية: $V = A' + \beta' e^{c' P(\%)}$

تكمن أهمية هذه العلاقات في إمكانية استعمالها لتحديد مسامية السبائك بدقة من أجل تطبيقات معينة. كما درسنا كذلك تأثير إضافة البورون على السرع الصوتية من اجل تحسين نوعية البائك المراد تطبيقها.

الكلمات المفتاحية: السبائك Ti-6Al-4V، السرعات الصوتية ، المجهرية الصوتية، ثوابت المرونة، المسامية.

Porosity Effects on Elastic Properties of Semiconductor Layers and Alloys

By: Yahya Al-Sayad

Abstract

In this work, we investigated several Ti-6Al-4V alloys that can be used as implants to replace different types of human bones. These alloys are characterized by their porous structure. Therefore, the porosity effects, P, on elastic Moduli (Young's, shear and bulk) as well as acoustic parameters (Reflection coefficient, acoustic response, longitudinal, transverse, Rayleigh velocities and acoustic impedances) have been investigated. The effects of porosities (up to 75%) were quantified for all cases; all parameters show an exponential decay with increasing porosities and relations were deduced. For elastic moduli, M, the dependence takes the form: $M = A + \beta\ e^{-c\ P\ (\%)}$ with A, β and c being characteristic constants. Whereas, for surface acoustic velocities, SAW, it is found that: $V = A' + \beta'\ e^{c' P(\%)}$. The importance of establishing such formula lies in their applicability to the prediction of the exact porosity for a given parameter and vice versa. Consequently, this allows the preparation of the required alloys for the replacement of a given bone types. Moreover, the effects of boron addition to Ti-6Al-4V alloys on SAW velocities have also been investigated; such additions improve the quality of the material.

Keywords: Ti–6Al–4V alloys, SAW velocities, Elastic constants, Acoustic microscopy, Porosity.

Effets de la porosité sur les Propriétés Elastiques des Couches et Alliages Semi-conducteurs

Par : Yahya Al-Sayad

Résumé

Dans ce travail, nous avons étudié plusieurs alliages Ti-6Al-4V qui peuvent utilisés comme implant pour le remplacement des os humains. Ces alliages sont caractérisés par leur structure poreuse. Ainsi, les effets de la porosité sur les modules élastiques (Young, cisaillement et volume) les paramètres acoustiques (coefficient de réflexion, signature acoustique, vitesses longitudinale, transversale, Rayleigh et impédances acoustiques) ont été étudiés. Les effets de la porosité (jusqu'à 75%) ont été quantifiés pour tous les cas ; tous les paramètres montrent une décroissance exponentielle et des relations on été déduites. Pour les modules élastiques, M, la variation prend la forme : $M = A + \beta\ e^{-c\ P\ (\%)}$ avec A, β et c des constantes caractéristiques. Pour les vitesses des ondes acoustiques de surface, il a été trouvé que $V_{SAW} = A' + \beta'\ e^{c' P(\%)}$. L'importance de ces formule réside dans leurs applicabilités pour la prédiction de la porosité exacte pour un paramètre donné et vice-versa. En conséquence, ceci permet la préparation des alliages demandés pour le remplacement d'un os précis. Par ailleurs, les effets de l'addition du boron aux alliages Ti–6Al–4V sur les vitesses des ondes acoustiques a été également étudiés ; ces ajouts améliore la qualité du matériau.

Mots clés: Alliages Ti–6Al–4V, Vitesses des ondes de surfaces, constantes élastiques, Acoustique microscopie, Porosité.

LIST OF SYMBOLS AND ABBREVIATIONS

Symbol	Definition
A(z)	*Attenuation material signal*
B	*Bulk Modulus*
BSE	*Backscattering electrons image mode*
$\mathbf{C_e}$	*Electronic Thermal Conductivity*
CIM	*Ceramic injection moulding*
$\mathbf{C_{ij}}$	*Stiffness Coefficient*
$\mathbf{C_L}$	*Lattice Thermal Conductivity*
$\mathbf{C_T}$	*Thermal Conductivity*
$\mathbf{C_v}$	*Heat Capacity*
$\mathbf{d_{ik}}$	*Piezoelectric Strain Constants*
$\mathbf{d_{ij}}$	*Piezoelectric Coefficients*
E	*Young's Moulus*
EBSD	*Electron backscattering diffraction*
EBSPs	*Electron backscattering diffraction Kikuchi patterns*
EDX	*Energy dispersive X-ray spectroscopy*
$\mathbf{e_{ik}}$	*Piezoelectric Stress Constants*
ELI	*Extra low interstitial*
f	*Acoustic Wave Frequency*
G	*Shear Modulus*
HDH	*Hydride-dehydride Ti powders*
HIP	*Hot isostatic pressing*
$\mathbf{l_{ph}}$	*Phonon Mean Free Path*
k	*Wavenumber in Coupling Fluid*
LEFM	*Linear elastic fracture mechanics*
LSR	*Linear shrinkage rate*
MIM	*Metal injection moulding*
MP	*Mill Powder with the addition of TiH2*
$\mathbf{n_i}$	*Propagation Direction in Crystal*
PIM	*Powder injection moulding*
PM	*Powder metallurgy*
PREP	*Powder Rotating Electrode Process*
|R|	*Modulus of Reflection Coefficient*

R(Θ)	*Phase of Reflection Coefficient*
SAM	*Scanning Acoustic microscopy*
SEM	*Scanning electron microscopy*
SHT	*Space Holder Technique in Powder Metallurgy*
SLPC	*Sintered loose and pressed conditions*
T	*Transmission coefficient*
UTS	*Ultimate tensile strength*
$\mathbf{u_i}$	*Displacement of an Arbitrary Point in the Solid*
$\mathbf{V_L}$	*Longitudinal Wave Velocity*
$\mathbf{V_{Liq}}$	*Sound Velocity in Liquid*
$\mathbf{V_R}$	*Rayleigh Wave Velocity*
$\mathbf{V_S}$	*Shear Wave Velocity*
V(z)	*Acoustic Material Signature*
Z	*Acoustic Impedance*
$\mathbf{Z_L}$	*Longitudinal Acoustic Impedance*
$\mathbf{Z_S}$	*Shear Acoustic Impedance*
γ	*Sommerfeld Parameter and*
Γ_{il}	*Second-rank Christoffel's Tensor*
δ_{ij}	*kroncal delta*
Δ**S**	*Growth of Solubility*
Δ**z**	*The Period of the Resulting Oscillations in V(z)*
θ_L	*Longitudinal Mode Critical Angle*
θ_R	*Rayleigh Mode Critical Angle*
θ_S	*Shear Mode Critical Angle*
λ	*Lamé Constant*
μ	*Lamé Constant*
ν	*Poisson Ratio*
ρ	*Material Density*
ρ_{ij}	*Specific Electric Resistance*
σ_y	*Yield strength*
χ	*Magnetic Susceptibility*
Λ	*Atomic occupation of planes*

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GENERAL INTRODUCTION

GENERAL INTRODUCTION

Despite the very early discover of Titanium in 1791, it is until 1940 that the first alloys, as well as the popular Ti-6Al-4V alloy were developed. The Ti-6Al-4V alloy is the most common used material among the commercially available titanium alloys. The reason for this success is the good balance of its properties and the intensive development and testing of this alloy during the approximately last 60 years [1]. Experiments were carried out in a challenge to determine the influence of critical features such as surface quality porosity on the behavior of Ti-6Al-4V alloys [2].

Ti6Al4V alloy are characterized by its porous structure which is a great advantage for this material to be be used as implants to replace different types of human bones. Nowadays,pPorous Ti-6Al-4V material alloys are successfully produced with porosities ranging from porosities (60% to 75%) under with compact pressures in the range from (100 to 450) MPa. Such alloys can be fabricated by several process techniques such as the production of Ti-6Al-4V foam by space holder technique in powder metallurgy, temperature 1080c°; particle size 400 µm [3].

It should be noted the mechanical properties of this ally is of great importance in its use as implants to support the necessary weight of a human being. It should be noted that elastic moduli of titanium alloys are much smaller than those of other metallic which use as biomaterials. They are however greater than that of bone, the moduli of recently developed β type alloys are between 55 to 85 GPa [4,5]. The effect of addition of Boron on Ti–6Al–4V alloys of the mechanical properties is also very important to understand the effects of simulated to changes of elastic modules to calculating of the acoustic materials signature curves. Whoever, body environment to the moduli of elasticity of biomedical titanium alloys on the mechanical properties [6].

Therefore, it would be very interesting to investigate elastic properties of Ti–6Al–4V alloys which are of major importance, since their measurement gives evidence about the forces that are performing between the fundamental atoms of a material. In this context, we investigate the porosity effects on elastic Moduli (Young's, shear and bulk) as well as acoustic parameters (Reflection coefficient, acoustic response, longitudinal, transverse, Rayleigh velocities and acoustic impedances) have been investigated. To do so, we considered some published data to simulate these effects in the case of a scanning acoustic microscopy. This technique has the advantage of being nondestructive, no contaminating method; it does not require prio-specimen preparation [7-10]. We determine analytical relations between porosity and all elastic parameters. The importance of this investigation lies in the prediction of the exact porosity for the best Ti-6Al-4V alloys to be used as implant in replacement of a given type of human bone (cortical, trabecular, etc.) Consequently, this allows the preparation of the required alloys for the replacement of a given bone types. Moreover, the effects of boron addition to Ti-6Al-4V alloys on SAW velocities have also been investigated; such additions improve the quality of the material.

This thesis is structured in three chapters. The first chapter concerns the background on biomaterials and titanium alloys. The physical properties and the porosity phenomena as well as the scanning acoustic microscopy are recalled in chapter 2. The last chapter is regroups all the results and discussion.

CHAPTER I

BIOMATERIALS AND Ti ALLOYS

I.1 INTRODUCTION AND BACKGROUND

Titanium, a transition metal which is well spread over the earth's crust, occurs in several minerals including rutile and limonite. Even though titanium is as strong as some steels, its density is only half of that of steel. Titanium is broadly used in a number of fields, including aerospace, power generation, automotive, chemical and petrochemical, sporting goods, dental and medical industries, [1–3]. The large variety of applications is due to its desirable properties; mainly the relative high strength combined with low density and enhanced corrosion resistance [4]. Among metallic materials, titanium and its alloys are considered the most suitable materials in medical applications because they satisfy the property requirements better than any other competing materials, like stainless steels, Cr-Co alloys, commercially pure (CP) Nb and CP Ta, [5–6]. In terms of biomedical applications, the properties of interest are biocompatibility, corrosion behavior, mechanical behavior, processability and availability, [7–9].

Titanium may be considered as being a relatively new engineering material. It was discovered much later than the other commonly used metals, its commercial application starting in the late 40's, mainly as structural material. Its usage as implant material began in the 60's, [10]. Despite the fact that titanium exhibits superior corrosion resistance and tissue acceptance when compared with stainless steels and Cr-Co-based alloys, its mechanical properties and tri-biological behavior restrain its use as biomaterial in some cases. This is particularly true when high mechanical strength is necessary, like in hard tissue replacement or under intensive wear use, [11]. To overcome such restrictions, Commercially Pure (CP) titanium was substituted by titanium alloys, particularly, the classic grade 5, i.e. Ti-6Al-4V alloy. The Ti-6Al-4V α+β type alloy, the most worldwide utilized titanium alloy, was initially developed for aerospace applications, [12, 13]. Although this type of alloy is considered a good material for surgically implanted parts, recent studies have found that vanadium may react with the tissue of the human body, [2]. Moreover, aluminum may be related with neurological disorders and Alzheimer's disease, [2]. To overcome the potential vanadium toxicity, Vanadium, a β-stabilizer element, was replaced by niobium and iron, while both alloys show mechanical and metallurgical behavior comparable to those of Ti-6Al-4V, a disadvantage is that they all contain aluminum in their compositions.

In recent years, several studies have shown that the elastic behavior of α+β type alloys is not fully suitable for orthopedic applications, [15–18]. A number of studies suggest that unsatisfactory load transfer from the implant device to the neighboring bone may result in its degradation, [9]. Also, numerical analysis of hip implants using finite element method, indicate that the use of biomaterials with elastic behavior similar to cortical bones improves the distribution of stress around the implanted bone, [19]. While the elastic modulus of cortical bones is close to 18 GPa, [7], the modulus of Ti–6Al–4V alloy is 110 GPa, [7]. In such a case, the high elastic modulus of the implant material may lead to bone resorption and possible unsuccessful implantation procedure. The elastic behavior mismatch between the implant and the adjacent bone is named "stress shielding effect" [19]. Since CP titanium and some specific α+β type titanium alloys do not completely meet the demands of medical applications, especially concerning mechanical behavior and toxicity to human body, a new class of alloys has been investigated for biomedical applications in the last decade, the β type alloys.

After proper heat treatments this type of alloys may exhibit low elastic modulus, very good corrosion resistance, suitable mechanical properties and good biocompatible behavior, as they may be obtained by adding biocompatible alloying elements like the microstructure diversity of titanium alloys is a result of an allotropic phenomenon. Titanium undergoes an allotropic transformation two new vanadium free α+β type alloys were developed in the 1980's. Leading to Ti-6Al-7Nb and Ti-5Al-2.5Fe α+β type alloys, Nb, Ta and Zr to titanium, [20–24].

This chapter, concerns some generalities on biomaterial: their use in the body as well as their applications we also recall some properties of metal and alloys with particular interest to mechanical properties.

I.2 USES OF BIOMATERIALS

Biomaterials are used to make devices to replace a part or a function of the body in safe, reliably economically, and physiologically acceptable manner. A variety of devices and materials are used in the treatment of disease or injury. Common place examples include suture needles, plates, teeth fillings, etc. [14].

I.2.1 Biomaterials in bodies

The science of biomedical materials involves a study of the composition and properties of materials and the way in which they interact with the environment in which they are placed. Materials can be used for different purposes according to their characteristics, advantages and disadvantages as summarized in Table I.1 [25, 26-31].

Table 1.1: Materials used in the Body [25]

Materials	Advantages	Disadvantages	Examples
Polymers (nylon, Si, Rubber, polyester, PTFE, etc.)	Resilient Easy to fabricate	Not strong Deformable with Degradable	Blood vessels, Sutures, ear, nose, Soft tissues
Metals (Ti and its alloys Co-Cr alloys, stainless Steels)	Strong Tough Ductile	May corrode, dense, Difficult to make	Joint replacement, Bone plates, pacer, Screws, dental root Implant, suture
Ceramics Al_2O_3, $Ca_3(PO4)_2$	Very biocompatible Inert strong in compression	Difficult to make Brittle Not resilient	Dental coating Orthopedic implants Femoral head of hip
Composites	Compression strong	Difficult to make	Joint implants Heart valves

Most biomaterials and medical devices perform satisfactorily, improving the quality of life for the recipient or saving lives. Still, man-made constructs are never perfect. Manufactured devices have a failure rate. Also, all humans differ in genetics, gender, body chemistries, living environment, and physical activity. Furthermore, physicians also differ in their "talent" for implanting devices. Table1.2 [25, 26-31] also reviews uses of Biomaterials.

Table 1.2: Uses of Biomaterials [26]

Uses of Biomaterials	Example
Replacement of damaged part	Artificial hip joint, kidney dialysis machine
Assist in healing	Sutures, bone plates and screws
Improve function	Cardiac pacemaker, intra-ocular lens
Correct functional abnormalities	Cardiac pacemaker
Correct cosmetic problem	Mastectomy augmentation, chin augmentation
Aid to diagnosis	Probes and catheters
Aid to treatment	Catheters, drains

I.2.2 Biomaterials in organs

Therapies for organ replacement transplantation replacement of tissue or organ from human or animal donor or cells grown on a scaffold device provide restored function (e.g., skin and cartilage) are also reviewed in Table1.3 [25, 26-31].

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Table 1.3: Biomaterials in organs [27]

Organ	Example
Heart	Cardiac pacemaker, artificial heart valve, Totally artificial heart
Lung	Oxy-generator machine
Eye	Contact lens, intraocular lens
Ear	Artificial stapes, cochlea implant
Bone	Bone plate, intra-medullary rod
Kidney	Kidney dialysis machine
Bladder	Catheter and stent

I.2.3 Selection of Biomedical Materials

The process of material selection should ideally be for a logical sequence involving: (i) analysis of the problem, (ii) consideration of requirement and (iii) consideration of available material and their properties leading to choose of material. Whereas, the choice of a specific biomedical material is determined by: (i) proper specification of the desired function for the material (ii) an accurate characterization of the environment in which it must function, and the effects that environment will have on the properties of the material, (iii) a delineation of the length of time the material must function and (iv) a clear understanding of what is meant by safe for human use. The most common classes of materials used as biomedical materials are polymers, metals, ceramics, composite materials, etc. These classes are used singly and in combination to form most of the implantation devices available today.

(a)- Polymer: There are a large number of polymeric materials that have been used as implants or part of implant systems. The polymeric systems include acrylics, polyamides, polyesters, polyethylene, poly-siloxanes, polyurethane, and a number of reprocessed biological materials. Some of the applications include the use of membranes of ethylene-vinyl-acetate (EVA) copolymer for controlled release. Some other typical biomedical polymeric materials applications include: artificial heart, kidney, liver, pancreas, bladder, bone cement, catheters, contact lenses, cornea and eye-lens replacements, external and internal ear repairs, heart valves, cardiac assist devices, implantable pumps, joint replacements, pacemaker, encapsulations, soft-tissue replacement, artificial blood vessels, artificial skin, and sutures. As bioengineers search for designs of ever increasing capabilities to meet the needs of medical practice, polymeric materials alone and in combination with metals and ceramics are becoming increasingly incorporated into devices used in the body.

***(b)- Metals*:** The metallic systems most frequently used in the body are:

- ✓ Iron-base alloys of the 316L stainless steel
- ✓ Titanium and titanium-base alloys, such as: (i)Ti-6% Al-4%V, and commercially pure ³ 98.9% and (ii) Ti-Ni (55% Ni and 45% Ti)
- ✓ Cobalt base alloys of four types: (i) Cr (27-30%), Mo (5-7%), Ni (2-5%), (ii) Cr (19-21%), Ni (9-11%), W (14-16%), (iii) Cr (18-22%), Fe (4-6%), Ni (15-25%), W (3-4%), (iv)Cr (19-20%), Mo (9-10%), Ni (33-37%)

The most commonly used implant metals are the 316L stainless steels, Ti-6%-4%V, and Cobalt base alloys of type "i" and "ii". Other metal systems being investigated include Cobalt-base alloys of type "iii" and "iv", and Niobium and shape memory alloys, of which (Ti 45% - 55%Ni) is receiving most attention. Further details of metallic biomedical materials will be given later.

(c)- Composite Materials: Composite materials have been extensively used in dentistry and prosthesis designers are now incorporating these materials into other applications. Typically, a matrix of ultrahigh-molecular-weight polyethylene (UHMWPE) is reinforced with carbon fibers. These carbon fibers are made by pyrolyzing acrylic fibers to obtain oriented graphitic structure of high tensile strength and high modulus of elasticity. The carbon fibers are 6-15 mm in diameter, and they are randomly oriented in the matrix. In order for the high modulus property of the reinforcing fibers to strengthen the matrix, a sufficient interfacial bond between the fiber and matrix must be achieved during the manufacturing process. This fiber reinforced composite can then be used to make a variety of implants such as intra-medullary rods and artificial joints. Since the mechanical properties of these composites with the proportion of carbon fibers in the composites, it is possible to modify the material design flexibility to suit the ultimate design of prostheses. Composites have unique properties and are usually stronger than any of the single materials from which they are made. Workers in this field have taken advantages of this fact and applied it to some difficult problems where tissue in-growth is necessary. We give some examples: deposited Al_2O_3 onto carbon, Carbon/PTFE, Al_2O_3/PTFE and PLA-coated Carbon fibers.

(d) – Ceramics: The most frequently used ceramic implant materials include aluminum oxides, calcium phosphates, and apatite's and graphite. Glasses have also been developed for medical applications. The use of ceramics was motivated by: (i) their inertness in the body, (ii) their formability into a variety of shapes and porosities, (iii) their high compressive strength, and (iv) some cases their excellent wear characteristics. Selected applications of ceramics include: (i) hip prostheses, (ii) artificial knees, (iii) bone grafts, (iv) a variety of tissues in growth related applications in orthopedics, dentistry, and heart valves. However, applications of ceramics are in some cases limited by their generally poor mechanical properties: in tension, load bearing, implant devices that are to be subjected to significant tensile stresses must be designed and manufactured with great care if ceramics are to be safely used.

(e) – Biodegradable Materials: Another class of materials that is receiving increased attention is biodegradable materials. Generally, when a material degrades in the body its properties change from their original values leading to altered and less desirable performance. It is possible, however, to design into an implant's performance the controlled degradation of a material, such that natural tissue replaces the prosthesis and its function. Examples include: suture material that hold a wound together but resorb in the body as the wound heals and gains strength. Another application of these materials occurs when they are used to encourage natural tissue to grow. Certain wound dressings and ceramic bone augmentation materials encourage tissue to grow into them by providing a "scaffold". The scaffold material may or may not resorb over a period of time but in each case, natural tissue has grown into the space, then by restoring natural function. One final application of biodegradable materials is in drug therapy, where it is possible to chemically bond certain drugs to the biodegradable material, when these materials are placed within the body the drug is released as the material degrades, thereby providing a localized, sustained release of drugs over a predictable period of time.

I.3 METALS AND ALLOYS

Metals are used as biomaterials due to their excellent electrical and thermal conductivity and mechanical properties. Since some electrons are independent in metals, they can quickly transfer an electric charge and thermal energy. The mobile free electrons act as the binding force to hold the positive metal ions together. This attraction is strong, as evidenced by the closely-packed atomic arrangement resulting in high specific gravity and high melting points of most metals. Since the metallic bond is essentially non-directional, the position of the metal ions can be altered without destroying the crystal structure, resulting in a plastically deformable solid. Some metals are used as passive substitutes for hard tissue replacement such as: (i) total hip, (ii) knee joints, (iii)or fracture healing aids as bone plates and screws, (iv) spinal fixation devices, (v) dental implants, because of their excellent mechanical properties, and corrosion resistance, (vi) vascular stents and (vii) catheter guide wires [34].

I.3.1 STAINLESS STEELS

Stainless steel was first used successfully as an important material in the surgical field.

- ✓ Type 302 stainless steel was introduced, which is stronger and more resistant to corrosion than the vanadium steel.

- ✓ Type 316 stainless steel was introduced, which contains a small percentage of molybdenum (18-8sMo) to improve the corrosion resistance in chloride solution.

- ✓ Type 316L stainless steel. The carbon content was reduced from 0.08 to a maximum amount of 0.03% for better corrosion resistance to chloride solution. The inclusion of molybdenum enhances resistance to pitting corrosion in saltwater. Even the 316L stainless steels may corrode in the body under certain circumstances in highly stressed and oxygen depleted region, such as the contacts under the screws of the bone fracture plate. Thus, these stainless steels are suitable to use only in temporary implant devices, such as fracture plates, screws and hip nails.

I.3.2 Co-Cr ALLOYS

There are basically two types of cobalt-chromium alloys:

- ✓ The Co Cr Mo alloy [Cr (27-30%), Mo (5-7%), Ni (2.5%)] has been used for many decades in dentistry, and in making artificial joints.
- ✓ The Co Ni Cr Mo alloy [Cr (19-21%), Ni (33-37%), and Mo (9-11%)] has been used for making the stems of prostheses for heavily loaded joints, such as knee and hip. The ASTM lists four types of CoCr alloys, which are recommended for surgical implant applications: (i) Co Cr Mo alloy [Cr (29-30%), Mo (5-7%), Ni (2.5%)]; (ii)Co Cr W Ni alloy [Cr (19-21%), W (14-16%), Ni (9-11%)]; (iii)Co Ni Cr Mo alloy [Ni (33-37%), Cr (19-21%), Mo (9-11%)]; (iv) Co Ni Cr Mo W Fe alloy [Ni (15-25%), Cr (18-22%), Mo (3-4%), W (3-4%), Fe (4-6%)].

The two basic elements of the CoCr alloys form a solid solution of up to 65% Co. The molybdenum is added to produce finer grains, which results in higher strengths after casting. The chromium enhances corrosion resistance, as well as solid solution strengthening of the alloy. The Co Ni Cr Mo alloy contains approximately 35% Co and Ni each. The alloy is highly corrosion resistant to seawater (containing chloride ions) under stress.

I.3.3 TITANIUM AND ITS ALLOYS

Titanium and its alloys are getting great attention in both medical and dental fields because of their: (i) Excellent biocompatibility, (ii) Light weight, (iii) Excellent balance of mechanical properties and (iv) Excellent corrosion resistance. They are commonly used for implant devices replacing failed hard tissue, for example, artificial hip joints, artificial knee joint, bone plate, dental implants, dental products (crowns, bridges and dentures) and used to fix soft tissue, such as blood vessels. In the elemental form, titanium has a high melting point (1668^{o}C) and possesses a hexagonal closely packed structure (hcp) a up to a temperature of882.5oC.Titanium transforms into a body centered cubic structure (bcc) b above this temperature. One titanium alloy (Ti6Al4V) is widely used to manufacture implants. The main alloying elements of the alloy are Aluminum (5.5-6.5%) and Vanadium (3.5-4.5%).

The addition of alloying elements to titanium enables it to have a wide range of properties:

- ✓ Aluminum tends to stabilize the a-phase; it increases the transformation temperature from α- to b-phase.
- ✓ Vanadium stabilizes the b-phase by lowering the temperature of transformation from a to β. He titanium-nickel alloys show unusual properties, that is, after it is deformed the material can snap back to its previous shape following heating of the material. This phenomenon is called (shape memory effect) SME. The equiatomic TiNi or NiTi alloy (Nitinol) exhibits an exceptional SME near room temperature: if it is plastically deformed below the transformation temperature it reverts back to its original shape as the temperature is raised. Another unusual property is superelasticity, which is shown schematically below in Fig.1.1. As can be seen the stress does not increase with increasing strain after the initial elastic stress or strain, the metal springs back to its original shape in contrast to other metals, such as stainless steel [35-37,41-45].

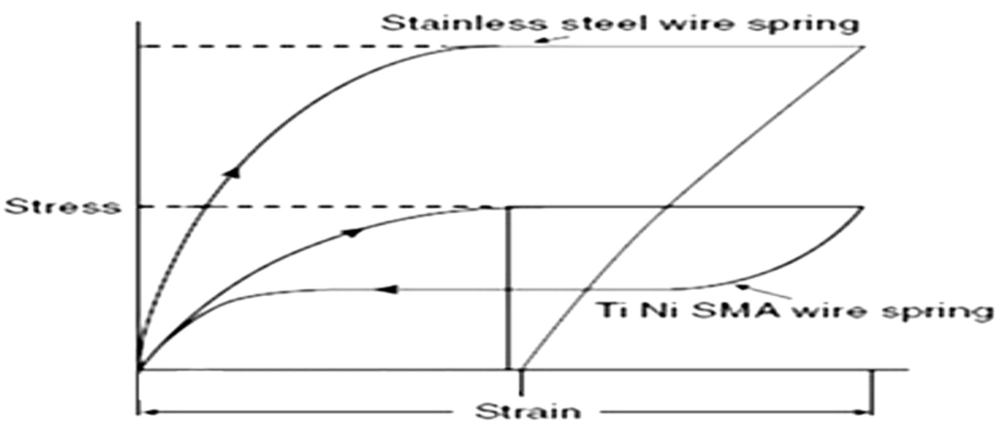

Fig.1.1: Schematic illustration of the stainless-steel wire and TiNi SMR wire springs for orthodontics arch-wire behavior [37,41.

I.4 BIOMEDICAL APPLICATIONS

The applications of titanium and its alloys can be classified according to their biomedical functionalities

1.4.1 Hard Tissue Replacement.

Hard tissues are often damaged due to accidents, aging, and other causes. Ti and Ti alloys are widely used as hard tissue replacements in artificial bones, joints, and dental implants. As a hard tissue replacement, the low elastic modulus of titanium and its alloys is generally viewed as a biomechanical advantage because the smaller elastic modulus can result in smaller stress shielding. One of the most common applications of titanium and its alloys is artificial hip joint that consists of an articulating bearing (femoral head and cup) and stem [35-37, 41-45] as in Fig.1.2. Titanium and titanium alloys are also often used in knee joint replacement, which consists of a femoral component, tibial component, and patella.

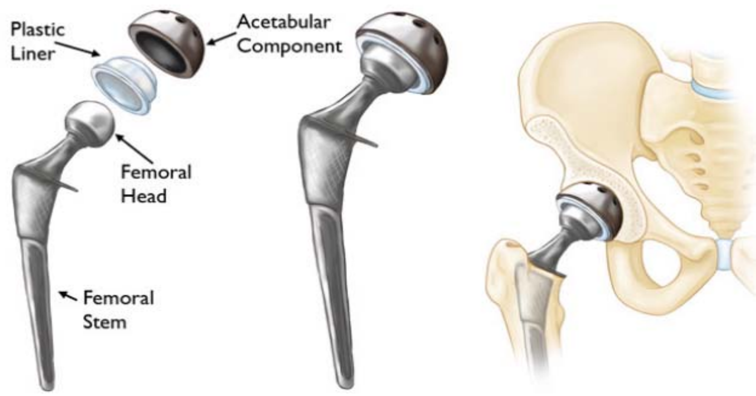

Fig.1.2: Schematic diagram of artificial hip join [35, 45]

Schematic diagram of artificial hip joint Titanium and titanium alloys are common in dental implants, the most commonly used implants are root-forming analogs. Fig.1.2 displays some of the popular designs, such as screw-shaped devices and cylinders.

1.4.2 Cardiac and Cardiovascular Applications.

Ti and Ti alloys are common in cardiovascular implants, because of their unique properties. Early applications examples were prosthetic heart valves, protective cases in pacemakers, artificial hearts and circulatory devices. Recently, the use of shape memory Ni-Ti alloy in intravascular devices, such as stents and occlusion coils has received considerable attention. The advantages of titanium in cardiovascular applications are that it is strong, inert and anon-magnetic. A disadvantage is that it is not sufficiently radio-opaque in finer structures.

1.4.3 Other Applications

Ti and Ti alloys are attractive materials in osteo-synthesis implant in view of its special properties that fulfill the requirements of osteo-synthesis applications. Typical implants for osteo-synthesis include bone screws, bone plates Fig.1.3, maxillofacial implants, etc [35-37, 41-45].

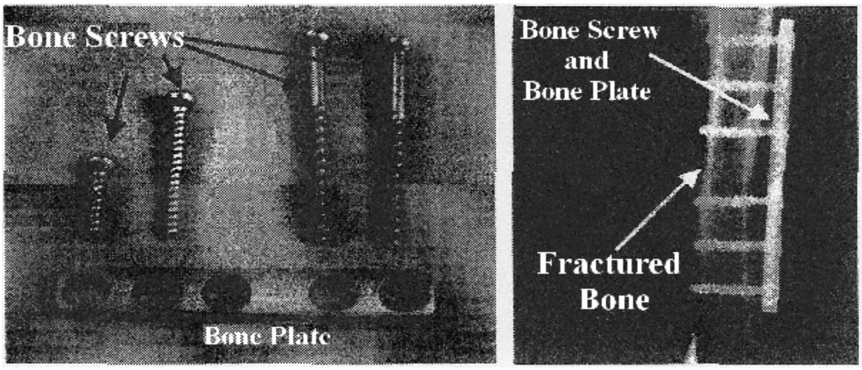

Fig.1.3: Bone screws and bone plate [36, 42].

I.5 SURFACE STRUCTURE AND PROPERTIES

1.5.1 Surface structure

There has been a considerable amount of scientific and technical knowledge published on the structure, composition, and preparation of titanium and titanium alloys, and many of the favorable properties arising from the presence of the surface oxide. It is well-known that a native oxide film grows spontaneously on the surface upon exposure to air. The excellent chemical inertness, corrosion resistance, passivation ability, and even biocompatibility of titanium and most other titanium alloys are thought to result from the chemical stability and structure of titanium oxide film that is typically only few nanometers thick. The characteristics of films grown at room temperature on pure titanium are summarized in Fig.1.4 [35-37, 41-45].

- ✓ The amorphous or nano-crystalline oxide film is typically 3-7nm thick and mainly composed of the stable oxide TiO_2;
- ✓ The TiO_2/Ti interface has an O to Ti concentration ratio that varies gradually from 2 to 1 from the TiO_2 film to a much lower ratio in the bulk;

- ✓ Hydroxide and chemisorbed water bond with Ti cations leads to weakly bound physio's orbed water on the surface. In addition, some organic species like hydrocarbons adsorb and metal-organic species, such as lakesides or carboxylates of titanium also exist on the outmost surface layer whose concentrations depend on not only the surface conditions,

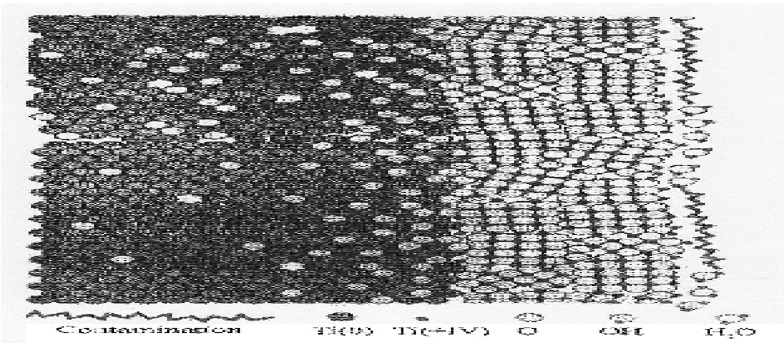

Fig.1.4: Schematic View of the oxide film on pure titanium [37, 45].

I.5.2 PROPERTIES

As far as mechanical properties are concerned, Titanium is very promising in orthopedics due to its high specific strength and low elastic modulus. However, titanium has low wear and abrasion resistance because of its hardness. Concerning biological properties, it should be noted that biocompatibility is the ability of the materials to perform in the presence of an appropriate host for a specific application. Thus, Ti and Ti alloys are generally regarded to have good biocompatibility. They are relatively inert and have good corrosion resistance because of the thin surface oxide. They typically do not suffer from significant corrosion in a biological environment. Titanium readily absorbs proteins from biological fluids. Titanium to bones has not been observed. Instead, the bond associated with osteointegrationist attributed to mechanical interlocking of titanium surface as pores in the bones. In order to make titanium biologically bond to bones, surface modification methods have been proposed to improve the bone conductivity or bioactivity of titanium[40-47]. The set of tables below (1.4, 1.5 and 1.6) summaries some examples of materials with their properties and applications.

Table.1.4: Biomaterials applications in internal fixation [35, 41].

Materials	Properties	Application
Stainless Steel	Low cost, easy fabrication	Surgical wire (annealed)
		Pin, plate, screw
		IM nail
Ti alloy	High cost	Surgical wire
	Low density and modulus	Plate, screws, IM nails
	Excellent bony contact	
Co-Cr (wrought)	High cost	Surgical wire
	High density and modulus	IM nail
	Difficult fabrication	
Polylactic acid	Resorbable	Pin screw
Polyglycolic acid	Weak strength	
Nylon	Non-resorbable plastic	Cerclage band

Table 1.5: Biomaterials for total joint replacements [35, 45]

Materials	Properties	Application
Co-Cr alloy	Stem, head (ball)	Heavy, hard, stiff
(casted or wrought)	Cup, porous coating	High wear resistance
	Metal backing	
Ti alloy	Stem porous coating	Low stiffness
	Metal backing	Low wear resistance
Pure titanium	Porous coating	Excellent osseous integration
Tantulum	Porous structure Good strength	Excellent osseous integration
Alumina	Ball, cup	Hard, brittle
		High wear resistance
Zirconia	Ball	Heavy and high toughness
		High wear resistance
UHMWPE	Cup	Low friction, wear debris
		Low creep resistance
PMMA	Bone cement fixation	Brittle, weak in tension
		Low fatigue strength

Table 1.6: Types of total joint replacements [37,44]

Joint	Types
Hip	Bull and Socket
Knee	Hinged, semi-constrained, surface replacement
	Uni-compartment or bio-compartment
Shoulder	Bull and Socket
Ankle	Surface replacement
Elbow	Hinged, unconstrained, surface replacement
Wrist	Ball and socket, space filter
Finger	Hinged, space filter

I.6 CHARACTERISTICS OF Ti AND Ti ALLOYS

Titanium is an early transition metal with an incomplete shell in its electronic structure, which enables the formation of solid solution .Titanium is an allotropic material with hexagonal close-packet (hcp) structure (α-Ti) and body-centered cubic (bcc) structure (β-Ti).the melting point is 1678C. Titanium alloys may be classified as α, near –α, α+β, detestable β, or stable β depending upon their microstructure at room temperature in this regard, alloying elements for titanium fall into three categories [36]:

- ✓ α stabilizers, such as Al, O,N,C.
- ✓ β stabilizers, such as Mo ,V, Nb, Ta.
- ✓ Neutrals, such as Zr.

The properties of Ti alloy materials depend on the composition, relative proportions of the α and β phases, thermal treatment and thermo-mechanical processing conditions. The Ti-Mn alloys have been used for hydrogen storage applications [37].

I.6.1 Ti element

The chemical behavior of Ti shows many similarities with that or silica and zirconium, as an element belonging to the first transition group. Its chemistry in aqueous solution, especially in the lower oxidation states, has some similarities with that of chrome and vanadium. Titanium is a transition metal light with a white-silvery-metallic color. It is strong, lustrous, and corrosion-resistant. Pure titanium is not soluble in water but is soluble in concentrated acids. This element burns in the air when it's heated up to obtain the dioxide, TiO_2, and when itis combined with halogens. It reduces the water vapor to form the dioxide and hydrogen, and it reacts in a similar way with hot concentrated acids, although it forms tri-chloride with chlorohydrin in acid. The metal absorbs hydrogen to give TiH_2, and forms the nitride, TiN, and the carbide, TiC. Other known compounds are the sulphur TiS_2, as well as the lowest oxides, Ti_2O_3 and TiO, and the sulphur's Ti_2S_3 and TiS. Salts are known in the three oxidation states.

I.6.2 Ti data

The data concerning Ti element as shown in Fig.1.5 are: atomic number 22, atomic mass 47.90 g.mol^{-1}, electro negativity according Pauling 1.5, density 4.51 g.cm^{-3} at 20°C, melting point 1660 °, boiling point 3287 °C, Vander Waals radius 0.147 nm. All the data of the physical, mechanical, optical and chemical properties can be found in *[29-32].*

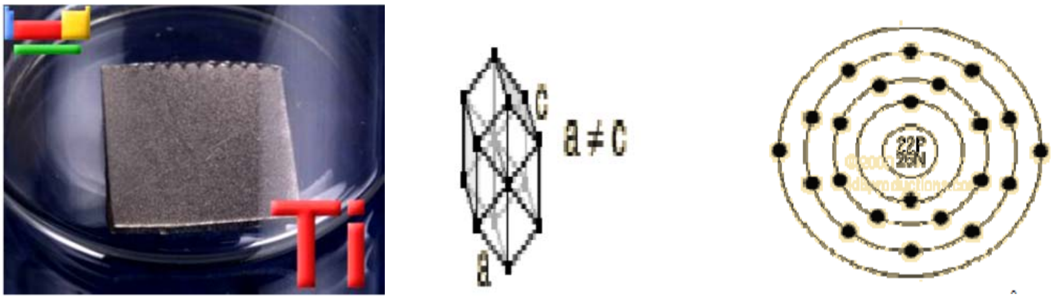

Fig.1.5: Titanium metal sample [29-32]

I.6.3 Alloying elements

The alloying elements can be categorized according to their effect on the stabilities of the α and β phases. Thus, Al, O, N and Ga are all α–stabilizers. Mo, V, W and Ta are all β-stabilizers. Cu, Mn, Fe, Ni, Co and H are also β-stabilizers but form the eutectoid. The eutectoid reaction is frequently sluggish (since substitution atoms involved) and is suppressed. Molybdenum and vanadium have the largest influence on ¯ stability and are common alloying elements. Tungsten is rarely added due to its high density. Cu forms TiCu2 which makes the alloys age–hardening and heat treatable; such alloys are used as sheet materials. It is typically added in concentrations less than 2.5 wt % in commercial alloys; Zr, Sn and Si are neutral elements.

I.6.4 Structure of Ti- alloys.

The microstructure diversity of titanium alloys is a result of an allotropic phenomenon. Ti undergoes an allotropic transformation at 882°C. Below this temperature, it exhibits hexagonal close-packed remains stable up to the melting point at 1,670°C, [5]. As titanium is (HCP) crystal structure, known as α phase, while at higher temperature it has a body-centered cubic (BCC) structure, β phase. The latter a transition metal, with an incomplete d shell, it may form solid solutions with a number of elements and hence, α and β phase equilibrium temperature may be modified by allowing titanium with interstitial and substitutional elements. Titanium alloying elements fall into three class: α-stabilizers, β-stabilizers and neutral. While elements defined as α-stabilizers lead to an increase in the allotropic transformation temperature, other elements, described as β-stabilizers provoke a decrease in such a temperature, [27]. When a eutectoid transformation takes place, this β-stabilizer is termed eutectoid β-stabilizer, otherwise, it is called isomorphous β-stabilizer. If no significant change in the allotropic transformation temperature is observed, the alloying element is defined as neutral element. Fig.1.6 shows a schematic representation of types of phase diagram between titanium and its alloys elements, [5, 37]. As a result, Ti alloys with an enormous diversity of compositions are possible. Among α-stabilizer elements are the metals of IIIA and IVA groups (Al and Ga) and the interstitials C, N and O. On the contrary, β-stabilizer elements include the transition elements (V, Ta, Nb, Mo, Mg, Cu, Cr and Fe) and the noble metals.

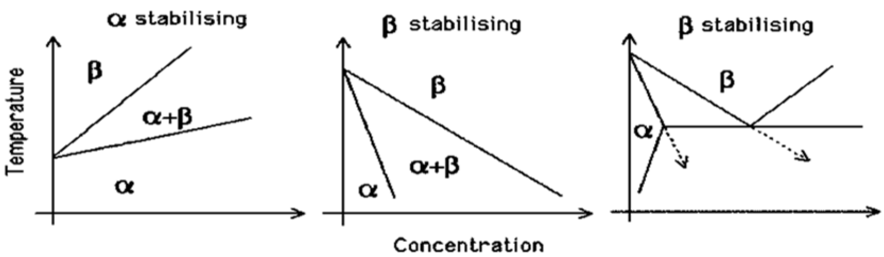

Fig. 1.6: Phase diagrams for Ti alloys [25]

I.7 MECHANICAL BEHAVIOR.

Concerning mechanical behavior, biomedical titanium alloys applied as biomaterial mainly in hard tissue replacement, must exhibit a low elastic modulus combined with enhanced strength, good fatigue resistance and good workability. Mechanical behavior of titanium alloys is directly related to composition and mainly, thermo-mechanical processing. Some mechanical properties of selected titanium-based materials applied as biomaterials are shown in Fig 1.7 [39]. Mechanical strength may be increased by adding alloying elements, which may lead to solid-solution strengthening or even, precipitation of second phases. Also, by using ageing processes, metastable structures obtained by rapid quenching from β field may give rise to fine precipitates, which considerably increases mechanical strength.

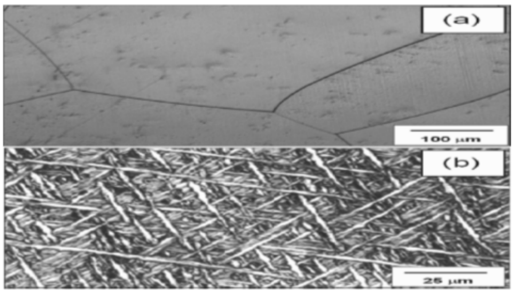

Fig. 1.7: Microstructures of (a) β Ti-35Nb (wt%) and (b) α+β Ti-6Al-7Nb (wt%) alloys cooled in air [40].

Titanium alloys present a high strength-to-weight ratio, which is higher than with most of steels. While CP titanium has yield strength between 170 (grade 1) and 485 MPa (grade 4), titanium alloys may present values higher than 1500 MPa [37]. The elastic modulus or Young modulus corresponds to the stiffness of a material and is associated to the way interatomic forces vary with distance between atoms in the crystal structure. A comparison between both crystal structures of titanium has led to the conclusion.

I.8 BIOMATERIAL APPLICATIONS OF Ti AND IT'S ALLOYS.

The field of biomaterials is of immense importance for the mankind as the very existence and longevity of some of the less fortunate human beings, who even at the time of birth are born with congenital heart disease and also for the aged population who require biomedical implants to increase their life span. The aged people need the help of geriatric physicians for several ailments as the parts of the human system have performed their expected tasks for long years and have become worn out. Arthritis is one of the major illnesses generally faced by the aged and even at times young people are also affected by this disease and it impairs

The life of those affected leading to immobility and unbearable pain. However, the cause of this disease remains unknown even today in spite of tremendous scientific advancements. Apart from diseased people, young and dynamic people like sportspersons often need replacements due to fracture and excessive strain. Currently, the availability of better diagnostic tools and advancements in the knowledge on materials as well as on surgical procedures, implant ology has assumed greater significance and bio implants are commonly used in dentistry, orthopedics, plastic and reconstructive surgery, ophthalmology, cardiovascular surgery, neurosurgery, immunology, histopathology, experimental surgery, and veterinary medicine Fig.1.8.

Various classes of materials such as metals, alloys, polymers ceramics and composites have been widely used to fabricate the bio implants. These implants encounter different biological environments of very different physic-chemical nature and their interaction with the tissues and bones is a complex problem. This requirement obviously demands a minimum service period of from 15 to 20 years in older patients and more than 20 years for younger patients. The success of a biomaterial or an implant is highly dependent on three major factors: (i) the properties (mechanical, chemical and tribological) of the bio-material in question (ii) biocompatibility of the implant and (iii) the health condition of the recipient and the competency of the surgeon.

The currently used materials that were selected based on above mentioned criteria though function well in the human system are still found to generally fail within a period of about 12-15 years, which leads to revision surgery in order to regain the functionality of the system. The reasons for their failure are manifold which includes mechanical, chemical, tri-biological, surgical, manufacturing and biocompatibility issues. Out of all these issues, the failure of an implant due to corrosion has remained as one of the challenging clinical problems. This important field of research, over the years, has been discussed at length by several authors in the form of books [43-45].and comprehensive review articles [46-48] and the interested reader can go through them to gain mastery over this subject.

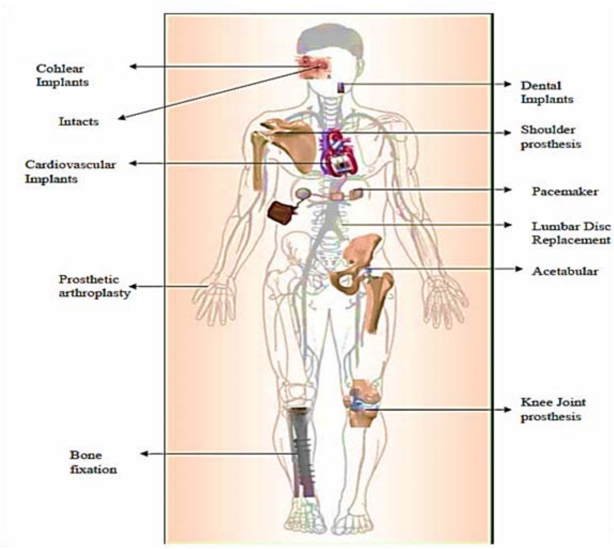

Fig. 1.8: Biomaterials for human application. [41-48].

I.9 CONCLUSION

The main property required of a biomaterial is that it does not illicit an adverse reaction when placed into services, that means to be a biocompatible material. As well, good mechanical properties, Osseo-integration, high corrosion resistance and excellent wear resistance are required. Material employed to replace the bone has similar mechanical properties to that of bone. The bone Young´s modulus varies in a range of 4 to 30 GPa depending on the type of the bone and the direction of measurement.

The development of new specialized surface modification techniques for titanium and its alloys is therefore an increasingly critical requirement in order to control or prevent these effects and improve Osseo-integration, hence extending the lifetime of the implant.

CHAPTER II

PHYSICAL PROPERTIES AND POROSITY OF Ti-6Al-4V ALLOYS

II.1 INTRODUCTION

Titanium-6Aluminum-4Vanadium is classified as one of the light alloys. It has a density 43% less than that of steel, yet with comparable strength. The Young's modulus for titanium is 120 GPa, versus 210 GPa for most steels and Co-based alloys. It has excellent corrosion resistance, forming a very stable layer of titanium oxide when exposed to air. Commercially pure (CP) titanium Ti has a hexagonal close packed (HCP) crystal structure below 882C° (α - phase). Above this temperature, the crystal structure transforms to body centered Cubic (BCC) atomic packing (β -phase).

The addition of aluminum as an alloying agent stabilizes the α -phase. Vanadium stabilizes the B - phase. Titanium alloy with 6% aluminum and 4% vanadium is the workhorse" alloy when high strength is required. Tensile strengths of over 1000MPa are attained with this alloy [1]. The addition of the alloying elements (6% Al and 4% V) raises the transformation temperature for Ti-6AI-4V to approximately 992 C°, at temperatures below 992 C°, a two-phase α+β structure forms. Ti-6AI-4V alloy is usually supplied in the mill annealed (MA) condition. It is produced by mechanical deformation just below 992 C° followed by a heat treatment at approximately 800 C° which is in the α+β field [2]. This comprises a mixture of both α phase and β phase in a fine grained, two-phase alloy. Equiaxed α-phase makes up the bulk of the alloy, with about 15% by volume of small β-phase particles, located primarily at the grain boundaries and triple points.

In this framework is a lack of studies around the real effect of this porosity on other important mechanical properties, i.e. elasticity modulus and SAW velocities behaviorism and also stiffness coefficients and acoustic impedance as well as the relationships between both the influences of leading porosity by governing (pressure- particle sizes – temperature). Different porosities at sintering temperatures they seem to us changes dynamic elastic moduli of bio-alloy. It was found that any increase in several porosity values Ti–6Al–4Valloy hints to a decreasing in different elastic constants elasticity modulus values and type of surface acoustic waves values; which may be caused by transitions crystal structure phases of Ti6Al4V alloy and manufacturing methods. In this context, we first recall the production of several Ti-6Al-4V alloys and their porosities. Then we summarize the scanning acoustic microscopy technique to be used in this work.

II.2 Ti-6AL-4V ALLOYS

Titanium was first discovered by the mineralogist and chemist, William Gregory in 1791. Four years later, Martin Klaproth, based on the story of the Greek mythological children, the Titans, named the element as titanium. After that, more than 100 years were necessary to isolate the titanium metal from its oxide. Finally, the first alloys, as well as the popular Ti-6Al-4V alloy, were developed in the late 1940s. The Ti-6Al-4V alloy is the most common used alloy among the commercially available titanium alloys [3]. Ti-6Al-4V alloy belongs to the group of α + β titanium alloys. The aluminum acts as a α stabilizer and the vanadium as a β stabilizer. At this specific composition both phases, α and β, are presented in the microstructure at room temperature. Typically, three different microstructure morphologies can be obtained by changing the thermo-mechanical processing route: fully lamellar structures, fully equiaxed structures, and bi-modal microstructures [4].

The most important parameter in the processing route is the cooling rate from β phase field during the recrystallization step since it delineates the size of the α lamellae, the α colony size and the thickness of the α layers at β grain boundaries. In the fully lamellar microstructure the α colony size, alternating α and β plates with distinct orientation relationship, is the feature that defines a grain, or in other words, the size of the slip length during plastic deformation. Thus, this feature determines mechanical properties such as tensile yield strength and high cycle fatigue strength. In the case of fully equiaxed Fig. 2.1b microstructure the typical thermo mechanical treatment is illustrated in Fig. 2.1a.

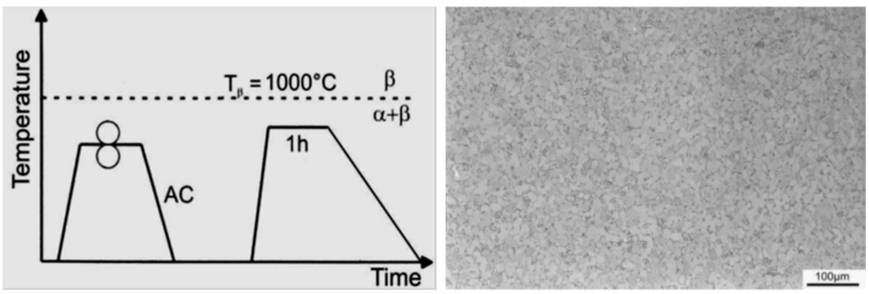

Fig. 2.1: *(a) illustrates the processing route for fully equiaxed microstructure, and (b) the resultant microstructure. [4].*

Again, the critical process segment is related to the cooling rate of the recrystallization process step. The cooling rate needs to be sufficiently low in order to allow only growth of α grains with no formation of α lamellae within the β grains, resulting in an equilibrium volume fraction of β phase located at the "triple-points" of the α grains. The microstructure feature that defines the grain size or the slip length for this microstructure is the α grain size.

II.3 TITANIUM AND ITS ALLOYS AS ORTHOPEDIC BIOMATERIALS

The need to find more reliable materials to replace broken or deteriorating parts of the human body is increasing with the increase in number of both younger and older recipients. Modern surgery and dentistry need metals and alloys of extreme chemical inertness and adequate mechanical strength. Metals and alloys in use include stainless steel, Co-Ni-Cr alloy, and cast and wrought Co-Cr-Mo alloy, CP titanium, Ti-6Al-4V alloy and other titanium alloys [12].

Recently, new titanium alloy compositions, specifically tailored for biomedical applications, have been developed. These first-generation orthopedic alloys included Ti-6Al-7Nb and Ti-5Al-2.5Fe. Two alloys with properties similar to Ti-6Al-4V that were developed in response to concerns relating V to potential cytotoxicity and adverse reaction with body tissues. Further, biocompatibility enhancement and lower modulus has been achieved through the introduction of second generation titanium orthopedic alloys including Ti-12Mo-6Zr-2Fe (TMFZ), Ti-15MO 5Zr-3Al, Ti-15Mo-3Nb-3O, Ti-15Zr-4Nb-2Ta- 0.2Pd and Ti-15Sn-4Nb-2Ta-0.2Pd alloys, as well as the completely biocompatible Ti-13Nb- 13Zr alloy [11]. CP titanium is a material of choice as an implant because of its biocompatibility resulting in no allergic reaction with the surrounding tissue and also no thrombotic reaction with the blood of human body. The average yield strength of commercially pure titanium is approximately 480 MPa. If a higher strength of the implant is necessary, for example, in hip prosthesis, titanium alloys have to be used. The most widely used alloy, Ti-6Al-4V, reaches yield strength almost double the yield strength of commercially pure titanium [12]. [13].

Ti alloys were first used in orthopedics in the mid-1940s and have continued to gain attention because of their unique properties, including high specific strength, light weight, excellent corrosion resistance and biocompatibility. Due to the aforementioned properties, this class of materials exhibits tremendous clinical advantages in terms of reduced recovery time and rehabilitation, and improved comfort for patients. However, for bone replacement components, the strength of pure Ti is not sufficient and Ti alloys are preferred due to their superior mechanical properties.

In general, alloying elements would lead to an improvement in the properties of Ti for orthopedic applications. Ti-6Al-4V ELI and NiTi shape memory alloys (SMA) are the most commonly used Ti alloys in orthopedic applications because of their good combination of mechanical properties and corrosion resistance. However, the possible release of toxic ions from Al, V and Ni during in vivo corrosion of the implant remains the matter of concern. Al for exceeding content of 7% at low temperature would lead to possible embrittlement and it may also cause severe neurological, e.g. Alzheimer's disease and metabolic bone diseases, e.g. osteomalacia. Similarly, V can alter the kinetics of the enzyme activity associated with the cells and results in potential cytotoxic effects and adverse tissue reactions. Moreover, the oxide layer of Al_2O_3 and VO_2 are less thermodynamically stable than that of TiO_2, as their harmful debris may take place in living organism. Evident cytotoxic and allergic responses of Ni have also been reported. Thus, it is necessary to develop new Ti alloys that contain non-toxic elements [10]. New Ti alloys are being introduced to change the chemical composition and the mechanical properties. Some of used Ti alloys as implant materials are listed in Table2.1.

Table 2.1: Some characteristics of orthopedic metallic implant materials [11]

	Stainless steels	**Cobalt-base alloys**	**Ti & Ti-base alloys**
Designatio	ASTM F-138 (316 LDVM)	ASTM F-75 ASTM F-799 ASTM F-1537 (Cast and wrought)	ASTM F-67(ISO 5832/II) ASTM F-136(ISO 5832/II) ASTM F-1295 (Cast and wrought)
Principal alloying Elements (wt%)	Fe(bal.) Cr(17-20) Ni(12-14) Mo(2-4)	Co(bal.) Cr(19-30) Mo(0-10) Ni(0-37)	Ti(bal.) Al(6) V(4) Nb(7)
Advantage	Cost, availability processing	Wear resistance Corrosion resistance Fatigue strength	Biocompatibility Corrosion Minimum modulus Fatigue strength
Disadvantages	Long term behavior High modulus	High modulus Biocompatibility	Power wear resistance Low shear strength

The properties in table 2.2 result from specific heat treatments and will vary depending on their processing parameters. Information in this table permits a comparison of mechanical properties of pure titanium, some alpha/beta titanium alloys and some beta titanium alloys [12]. The biocompatibility performance of a metallic alloy is closely associated with its corrosion resistance and the biocompatibility of its corrosion products. Corrosion data show excellent resistance for titanium and its alloys though some precautions should be taken in order to optimize their composition [14].

Table 2.2: Mechanical properties of selected titanium alloys [14]

Type, Alloy,	**E**	**UTS**	**YS (0.2%)**	**%**	**%Red**
Nominal wt.%	**GPa**	**MPa**	**MPa**	**E1**	**Area**
Alpha Ti	105	240-617	165-520	12-27	
Alpha/Beta Ti-6a1-4V	88-116	990-1184	789-1013	2-30	2-41
Ti-5A1-2.5Fe	110	943-1050	818-892	13-16	33-42
Ti-6A1-7Nb	108	900-1100	910-970	11-14	
Beta Ti-13Nb-13Zr	79	550-1035	345-932	8-15	15-30
Ti-11.5Mo-6zr-2Fe	74-85	1060-1100	910-970	18-22	46-73
Ti-15Mo-5Zr-3Al	15-113	882-1312	870-1284	11-20	43-83
Ti-15Mo-3Nb	79	1035	993	15	60

Alloy design and thermo-mechanical processing control of Ti alloys has allowed the production of implant materials with enhanced properties. Ti and its alloys are used in orthopedic surgery as implants in the shape of wires, nails, plates and screws for fixation and stabilization of fracture or in the form of artificial joints for the replacement of joints of the human body. Some implants are used for short time duration in the human body whereas others remain in place providing a continuous and trouble-free function for decades. To avoid a reoperation caused by the implant material, the material must meet certain chemical and mechanical requirements. As previously mentioned, chemical requirement includes high biocompatibility without altering the environment of the surrounding tissue even under deformation and sterilization. Mechanical property requirement relates to specific strength, modulus, fatigue, creep and fracture toughness which, in turn, relate to microstructures. The direct relation of the microstructure to properties and performance makes it necessary that the microstructural condition be part of the specification for a finished device [13].

In general, most of the Ti alloys offer appropriate mechanical properties for orthopedic applications. The modulus of Ti alloys is closer to those of bone and theoretically provides less stress shielding than those of stainless steel and Co-Cr alloys. Fig. 2.2 presents elastic moduli of some important materials used in bone tissue engineering. The Young's moduli of 316L stainless steel and Co–Cr–Mo alloy are much greater than that of cortical bone. The Young's moduli of biomaterials have been said to be desirable to be equal to that of cortical bone because if the Young's moduli of biomaterials are much greater than that of cortical bone, bone resorption occurs. The Young's modulus of α + β type titanium alloy, Ti–6Al–4V that is the most widely used titanium alloy for biomedical applications, is much lower than those of stainless steel and Co based alloy. However, its Young's modulus is much greater than that of cortical bone [15].

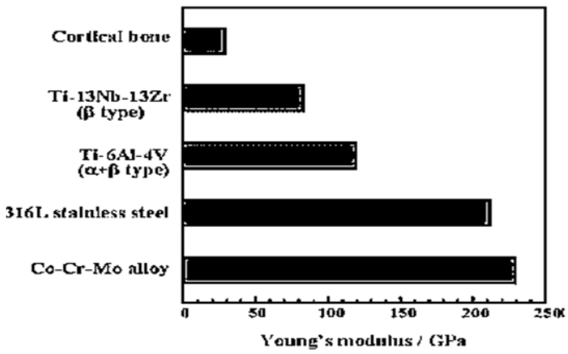

Fig.2.2: Comparison of Young's modulus of cortical bone, β type Ti–13Nb–13Zr, α + β type Ti–6Al– 4V, 316L stainless steel and Co–Cr–Mo alloy for biomedical applications [15].

II.4 Ti PRODUCTION

Ti is present in several minerals, sand, rocks and is normally found as a rutile (TiO2) and ilmenite ($FeTiO_3$). In the 1940's an inexpensive metallurgical process was introduced known as extended 'Kroll process' to reduce TiO_2 to metallic Ti in order to give a similar concentration of TiO_2 comparable to rutile. Titanium tetrachloride is formed with the added of Chlorine and then magnesium is used for final reduction, as show Fig.2.3. The magnesium chloride formed by this reaction is subsequently electrolyzed to reduce it to magnesium and chlorine which is recycled contributes to cost reduction. The final purity of the sponge is determined by the level of magnesium contamination and the reaction with the reactor walls. Further processing converts titanium sponge into an ingot.

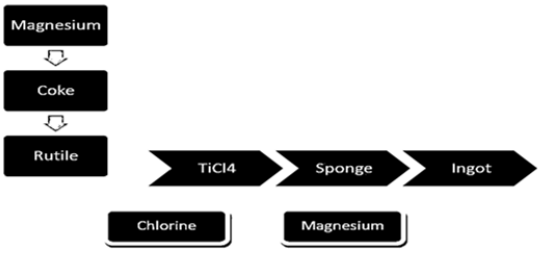

Fig.2.3: Flow Chart and mass balance sheet for titanium product fabrication from ore [16].

The ingot is formed through multiple re-melting processes. This re-melting is necessary in order to achieve high purity Ti by reducing remaining magnesium and chlorides. However, the higher purity titanium has poor strength and is not used for industrial applications. The alloy composition desired is set during the transformation from titanium sponge to ingot. Ti sponge is pre-densified in a hydraulic press to form a compact of pure titanium. The compacts, adequately alloyed, are then assembled into an electrode for multiple melting processes via vacuum arc melting (VAC). Due to high oxygen Ti affinity, the compacts must be welded under argon in a plasma welding to form an electrode.

Production of titanium is mostly done through single, double and triple vacuum arc melting in a vacuum chamber. The self-consuming electrode consists of the compact predefined Ti alloys. An arc is formed between the electrode and some dwarf placed at the bottom of the water-cooled crucible. As a result of a high arc energy, the self-consuming electrode is melted and forms an ingot in the crucible. The melting temperature, cooling water and the electrode gaps are essential to for the effective control of the process and production of defect free material [16]. Among other methods are (i) Plasma Rotating Electrode Process (PREP), (ii) Gas Atomization Process, (iii) Hydride Dihydride Process, (iv) Mechanical alloying and (v) Powder metallurgy.

II.5 CLASSIFICATION OF Ti ALLOYS

Ti, as a transition metal, has incomplete electronic structure in its outer shell that enables Titanium to form solid solutions of both substitutional and interstitial kinds. The classification of Ti alloys is normally based on the influence of alloying elements. This is because the alloying of Ti is dominated by the ability of elements to stabilize either of the α – or the β- phases [18].

Depending on their influence on the β-transus temperature, the alloying elements of Ti are classified as:

(a) Neutral: Neutral alloying elements have a minor influence on the titanium transformation temperature. Sn and Zr are falls into this category but as far as strength is concerned they are not neutral since they primarily strengthen the α-phase.

(b) α-stabilizers: α-stabilizing elements extend the α phase field to higher temperature and while extending the α phase field, the α-stabilizers develop a two phase α+β field. Of these, the α-stabilizing elements are subdivided into β isomorphs and β eutectic elements. Al and interstitial elements such as O, N and C belong to this category.

(β) Stabilizers: β - stabilizing elements shift the β phase field to a lower temperature. Fe, Mn, Cr, Co, Ni are among the β stabilizing elements; Al and O are the most important elements that preferentially will dissolve in the α phase and expand the ß transus to higher temperature. The addition of Sn and Zr elements do not influence the transus temperatures and are categorized categorize as neutral elements. Vanadium is a common ß stabilizing. Hence, Ti alloys can be classified according to their microstructure. These are (a) α alloy, (b) near α alloy, (c) α+ß alloys, (d) near ß alloys and (e) metastable ß.

II.6 Ti-6AL-4V MICROSTRUCTURE

Microstructure refers to the phases and grain structure present in a metallic component. Ti6Al4V is an α+ ß alloy containing 6 wt % of Al and 4 wt % of V. This titanium alloy is formed when a blend of alpha favoring (Al) and beta favoring (V) alloy elements is added to Ti. A wide variety of microstructure can be generated in alpha-beta alloys by adjusting the thermo-mechanical processing parameters. The transformation of an alpha structure to beta structure upon heating is complete if the heating temperature goes above the ß-transus temperature. Upon the subsequent cooling, the beta structure will change back to alpha with a small amount of Beta (depends on the quantity of ß-stabilizers elements) as untransformed beta at room temperature. The alpha phase present during cooling, which is primary alpha, can remain relatively globular (equiaxed), however the transformed beta (marten site or alpha) can be very acicular or elongated. The amount of alpha phase and the fineness or coarseness of this final microstructure will affect the behaviour of this titanium alloy [18, 19].

II.7 ADVANTAGES OF Ti ALLOYS

The application of Ti alloys has expanded from the aerospace industry, automotive to the medical industry. Although the materials themselves are considered to be expensive materials, the physical properties are desirable for high end products and under elevated temperature conditions. The mechanical properties such as strength, ductility, creep resistance, fracture toughness and crack propagation resistance depend essentially on the microstructure, which is formed during thermo-mechanical processing and thermal treatment procedures. The main advantages of Ti alloys are;

- ✓ Higher strength to weight ratios.
- ✓ Low densities, which fall between aluminum and iron and give attractive strength to weight ratios allowing lighter and stronger structure.
- ✓ Superior corrosion and erosion resistance in many environments, in particular to pitting and stress corrosion cracking.
- ✓ High temperature capability in the range of 300-400: ^{o}C.
- ✓ High toughness, which is useful for making precision mechanism gears, turbine engine components and biomedical prosthesis devices.

II.8 MORPHOLOGY AND CHEMICAL COMPOUNDS

The morphology of the Ti6Al4V gas atomized powder was examined through the optical microscope and the scanning electron microscope. The chemical compounds were investigated using Electron Dispersive Spectroscopy (EDS). Generally, all the powder particles were spherical. A few irregular particle shapes were seen in the powder sample due to vibration and rough handling, as shown in Fig.2.4. It was also noted that the powder particles were of a small size with an average of 50 microns. From the elemental analysis, no other elements were detected besides the titanium, aluminum and vanadium, confirming a lack of chemical contamination on the surface [17]. The powder density was calculated via the gas psychometry apparatus. Based on the Ti6Al4V reference density of 4.46 g/cm^3 [18]; the laser sintered of Ti6Al4V has 98.65% relative density which is considered as near to full density.

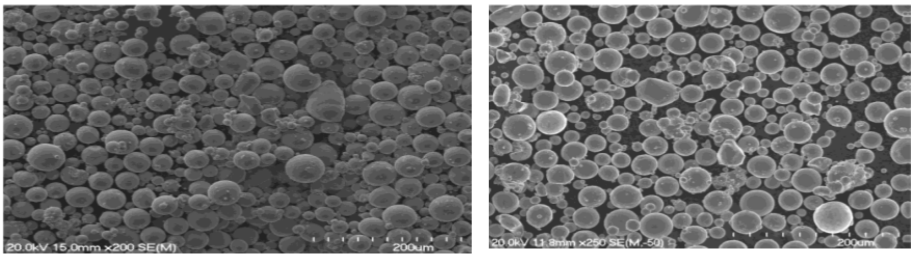

Fig.2.4: Ti6Al4V Powder particles via SEM [17]

II.9 POROSITY

Porosity is a measure of the void spaces in a material, and is measured as a fraction, between zero and unity, or as a percentage between 0 – 100%. The term is used in multiple fields including ceramics, metallurgy, materials, manufacturing, earth sciences and construction.

II.9.1 Porosity measurements

Several methods can be employed to measure porosity, including the volume/density method (pore volume = total volume - material volume), water saturation method (pore volume = total volume of water - unsaturated water), water evaporation method (pore volume in cubic centimeters = weight of saturated sample in grams - weight of dried sample in grams),mercury intrusion primary (several non-mercury intrusion techniques have been developed due to toxicological concerns, and the fact that mercury tends to form amalgams with several metals/alloys), and nitrogen gas adsorption (nitrogen gas adsorption in pores is measured either by volume or weight; this technique is suitable for materials with very fine pores). The density of composite materials used to precisely measure Archimedes law, the application of electronic analytical balance measurements, uses the formula [20].

$$\rho = \left(1/\left(\frac{A\%}{\rho A}\right) \pm \left(\frac{B\%}{\rho B}\right)\right). \qquad (2.1)$$

where *A%*、*B%* Composite per million each element of the quality of the percentage, ρA *and* ρB the corresponding components of the material element of the theoretical density (g/cm^3).

Relative density is given by the formula**:**

$$d = \rho/\rho_0 \text{ x } 100\% \tag{2.2}$$

where ρ is the alloy density of alloy and ρ_0 is the non-porous value.

Porosity of alloys, P, for different temperatures can be written as:

$$P = (M2-M1)/(M3-M2). \tag{2.3}$$

where M2 is weight alloy in Air (dry before boiled water), M1 is weight alloy in Air (dry after boiled water) and M3 is weight alloy in Air (wet after boiled water).

II.9.2 Porosity types

Many applications require that a medium, either liquid or gaseous, be able to pass through the cellular material. In this case open porosity is required for high rate of fluid flow. Figure 2.5 shows different types of porosity as (i) well-sorted classic sediment of high primary porosity, (ii) poorly sorted classic sediment of restricted primary porosity and (iii) well-sorted classic sediment with extremely high primary porosity. Due to the porous character of the grains, we have: (i) well-sorted classic sediment with cement infill of the primary porosity, (ii) secondary porosity due to solution and (iii) secondary porosity along fractures in a fractured rock.

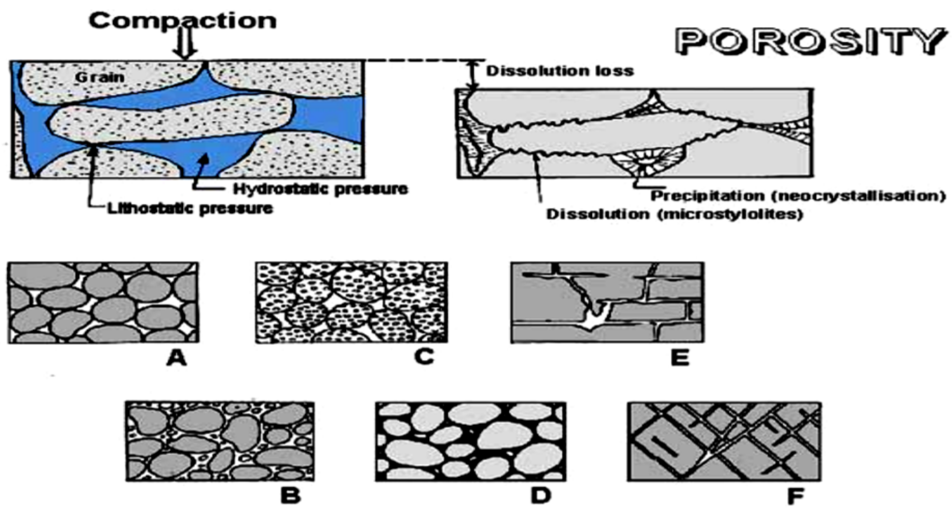

Fig. 2.5: Schematic diagram of porosity types.

II.9.3 Porous Ti-6Al-4V alloys

Ti-6Al-4V alloys are the most important metallic materials used in the biomedical applications due to their excellent mechanical properties and superior biocompatibility. However, there some problems about the titanium implants in orthopedic surgery such as the mismatching of titanium and natural bone properties [21, 22]. It is known that the mechanical properties can be controlled through the manufacturing of a porous sample. The porosities should be controlled by (Pressure –Temperature- particle size) to obtain porosities up to 75% to simulate the human cancellous bone and cortical Bones have porosities 35%.

Several porous Ti-6Al-4V alloys that led to equivalent elastic modulus of human bones (0.1to40) GPa can be cited:

- Porosities ranging from porosities (61% to 75%) with compaction pressures in the range from (100 to 450) MPa. Production of Ti-6Al-4V Foam by Space Holder Technique in Powder Metallurgy, Temperature 1080C°; particle size 400 µm [23].
- Porosities (58% to 62%) prepared using space holder method with two different Ti64 powders under Pressure 400 MPa, Temperature (1200-1350)°C; particle size (45-154,30-90) µm, [24, 32].
- Porosities, (20% to 60%) fabricated by powder metallurgy process with the addition of TiH_2 as the pore forming and active agent. under Pressure (9-88) MPa; Temperature (840-1100) C°; particle size (900-190) µm, [25].
- Porosities (25% to 31%) under Pressure (375-1125) MPa; Temperature (850-1250) C°; particle size (45-150) µm Young's Moduli values for minimum and maximum porosities obtained from sintered samples in loose and pressed conditions. [26].
- Porosities (30% to 37%) produced by sintering of powders in loose condition and powder rotating electrode process (PREP) under Pressure (375-1125) MPa; Temperature (800-1250) C°; particle size (200-500) µm [27].
- Porosities (35% to 70%) fabricated by a space-holder and powder metallurgy method. under Pressure 450 MPa; Temperature 1200 C°; particle size (560-1000) µm [28].

II.10 MECHANICAL PROPERTIES OF USED MATERIALS

It is established that increasing porosities of Ti–6Al–4V alloy lead to variations of Young's modulus, shear modulus, bulk modulus, longitudinal velocities, shear velocities and Rayleigh velocities, stiffness coefficients and acoustic impedance; this phenomenon would influence the choice of hard tissue replacement for human bones have elastic modulus (0.1 to 40) GPa [21, 22-28].

Porous Ti-6Al-4V alloys used successfully as implants possess porosities in the range (61% to 75%) with compaction pressures in the interval (100 to 450) MPa. The Ti-6Al-4V foam is produced by Space Holder Technique in Powder Metallurgy, temperature 1080°C; particle size 400 µm [23]. Typical elastic constants with varying porosities tested under pressures and temperatures are shown in Table 2.3. The non-porous annealed Ti-6Al-4V is characterized by E = (110-114) GPa and σ = 0.34 with a density = 4430 g/cm^3 [29].

Table 2.3: Parameters of Ti-6Al-4V alloys with vary process techniques. [21, 22].

Ti-6Al-4V alloys						
Porosity (%)	**61 - 75**	**58 - 62**	**20 - 60**	**25 - 31**	**30 - 37**	**35 - 70**
Pressure (MPa)	100 - 450	400	9-88	375-1125	375-125	450
Temperat. (C°)	1080	1200-1350	840-1100	850-1250	850-250	1200
Particle size (µm)	400	(45-154) (30 - 90)	900-190	45-150	200-500	560-1000
Technique	Space holder	space holder	MP with TiH2 addition	Sintered loose and pressed conditions	(PREP)	space-holder and powder metallurgy method
Density (gcm-3)	4430	3290	4480	2710	2710	4430
Poisson ratio σ	0.325	0.325	0.342	0.328	0.328	0.325
E(GPa)	3.8 to 0.25	2.5 to 1.77	24 to 4	64 to 11.1	14 to 3.9	19 to 11

II.11 SCANNING ACOUSTIC MICROSCOPY

II.11.1 Instrumentation

Non-destructive acoustic investigations are based on the emission and reception of SAWs that interact with the elastic properties of a given material where different modes propagate. Among the most promising tools that have demonstrated a variety of unique capabilities in qualitative and quantitative characterization of surface and sub-surface details are scanning acoustic microscopes, SAM, [30-35]. The SAM can be operated either in reflection or in transmission.

- ✓ Reflecting acoustic microscope: The transmitter system (the transducer) also acts as a receiver by using the inverse piezoelectric effect (the emitted and reflected signals are then separated in time). The reflection SAM is the most widely used instrument.
- ✓ Transmission acoustic microscope: A transducer-transmitter is a transducer-receiver that simultaneously scans the two parallel faces of the sample (at the surface or at depth).

The reflection scanning acoustic microscope, SAM, consists of several parts:

- ✓ Mechanical part: he acoustic image is obtained by mechanical scanning of the sample with respect to the sensor (or the opposite) in two perpendicular directions (x, y) in the focal plane of the lens.
- ✓ Electronic part: the information received at the output of the transducers is digitized and then stored in a memory in correspondence with the movements of the object. The final image is visualized on a conventional monitor with magnifications ranging from a few units to around 2000.
- ✓ Acoustic part (Fig. 2.6): This is the emission and reception part of the acoustic wave. It consists of the piezoelectric transducer (ultrasonic generator), the delay line (propagation medium), the acoustic lens (focusing element), the coupling fluid for the transfer of ultrasonic waves and the sample to be studied.

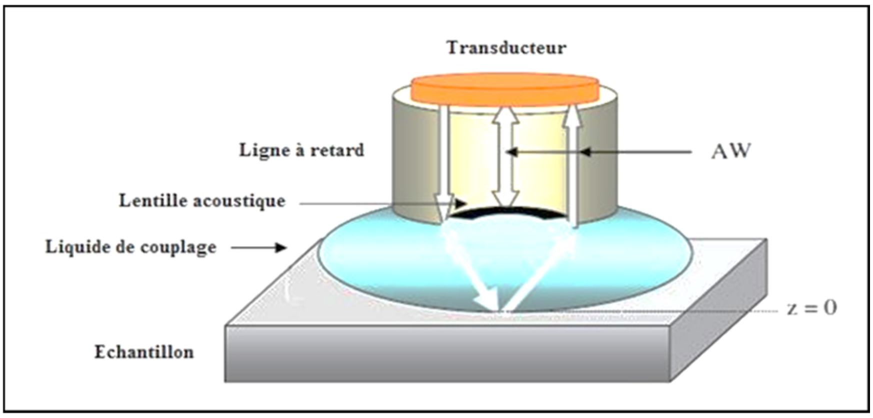

Fig 2.6: Schematic diagram of the acoustic part of a SAM. [35].

II.11.2 SAM Principle and methodology

The principle of an acoustic microscope is to generate a very high frequency ultrasonic wave (tens or even hundreds of MHz) by a transducer subjected to a variable electrical excitation. The sound wave emitted is focused by a delay line and then sent to a sample (the structure to be controlled) through the coupling liquid. The sample is initially placed in the focal plane of the lens and will then be moved vertically and / or horizontally by a system of mechanical motors. This wave (reflected or transmitted) is then received and converted into an analog signal (electrical voltage), which can be easily measured and converted into an image.

Non-destructive ultrasonic methods usually consist of determining SAW velocities (longitudinal, V_L, transverse, V_T and Rayleigh, V_R.) from which elastic constants are deduced according to well established conventional relations and vice versa. These velocities can be determined, in the recent scanning acoustic microscopy technique, from the so-called acoustic material signatures, also known as V(z) response. Such a signature describes the output response, V, as a function of the defocusing distance, z, in acoustic microscopy configuration. For modelling sake, the V(z) signature is given, via the angular spectrum model, by Sheppard and Wilson formula [36].

$$V(z) = \int P^2(\theta)R(\theta)\exp(2jk_o z\cos\theta)\sin\theta\cos\theta d\theta \qquad (2.4)$$

Here $P^2(\theta)$ is the pupil function, $R(\theta)$ is the reflection coefficient, θ is the half-opening angle of the lens, z is the defocusing distance and $k_o = 2\pi/\lambda$ is the wave number in the coupling liquid and $j = \sqrt{-1}$.

Acoustic materials signatures, thus deduced, possess an oscillatory behavior as a result of constructive and destructive interference between different propagating modes. Therefore, their treatment can be carried out via Fast Fourier Transform, FFT, which exhibit a large spectrum consisting of one or several peaks. The most dominant mode (usually Rayleigh) appears as a very sharp and pronounced peak from which the velocity of the can be determined [37] according to:

$$V_R = V_{liq.}/[1 - (V_{liq.}/2f\Delta z)^2]^{1/2} \tag{2.5}$$

where V_{liq} is the sound velocity in the coupling liquid, f is the operating frequency of the transducer and Δz the periods in V(z) curves.

The methodology consists of:

(i) determining SAW velocities of different modes,
(ii) calculating acoustic materials signatures,
(iii) determining Rayleigh velocity via FFT treatment of periodic V(z) signatures,
(iv) repeating steps (i) to (iii) for each alloy.

II.12 CONCLUSION

Titanium continues to be widely used for implant and biomedical applications. Titanium alloys have a high strength to weight ratio with a density. Their excellent corrosion resistance in many environments is due to the formation of a stable oxide surface layer. The most commonly used titanium alloys is Ti-6Al-4V, due to their excellent corrosion resistance, tensile strength, a high strength to weight ratio and low elastic modulus. However, their mechanical properties are greatly affected by the degree of porosities which are of great importance in many device applications. Thus, the state of the art of Ti and its alloys is described in this chapter as well as the scanning acoustic microscopy which is a nondestructive technique that could be used in the investigation of these materials

CHAPTER III

RESULTS AND DISCUSSIONS

III.1 INTRODUCTION

The physical properties of Ti-6Al-4V alloys materials have been widely studied but their elastic properties are poorly investigated. Hence, in this chapter, we examine elastic properties of Ti-6Al-4V alloys with varying porosities at different parameters such as various sintering temperatures and pressures [1-5]. The effects of these parameters on mechanical properties of Ti-6Al-4V alloys are very important in many device applications and in fundamental understanding. The mechanical properties of titanium and titanium alloys are very sensitive to human bones have elastic modulus (0.1 to 40) GPa, which should have porosity up to 75% to simulate the human cancellous bone and cortical Bones have porosities 35% [6-9].

Hence, we first deduce the values of propagating surface acoustic wave, SAW, velocities as well as bulk modulus, B, Poisson ratio, for Ti-6Al-4V alloys. Then calculate reflection coefficients as well as acoustic materials signatures of Ti-6Al-4V alloys at porosity (61% to 75%) Ti-6Al-4V alloys with compaction pressures in the range from (100 to 450MPa). The considered materials were produced by Space Holder Technique in Powder Metallurgy, Temperature 1080C°; particle size 400 µm [1].

III.2 MECHANICAL PROPERTIES OF Ti-6Al-4V ALLOYS

Elastic properties of 0% non-porous Ti-6Al-4V were reported in literature [2]. The parameters of this materials were found to be E = 110 –114 GPa, ρ = 0.34, V_L = 635 m/s, V_S = 3152m/s and V_R = 3060 m/s; the whole parameters are summarized in Table 3.1.

Table 3.1: Properties of Ti-6Al-4V alloy. [2].

property	Porosity (%)	Density (gcm^{-3})	Elastic modulus (GPa)	Poisson ratio
Ti–6Al–4V Annealed	0	4430	110–114	0.34

Porosities (%)	Moduli (GPa)			Velocities (m/s)			stiffness coefficients (GPa)			Acoustic impedance (M rayl)		
P	E	G	B	V_L	V_T	V_R	C11	C12	C44	Z_L	Z_T	Z_{solid}
0	110 to 114	45 to 50	102 to 107	6351 to 6355	3152 to 3156	3060 to 3064	210 to 214	120 to 124	81 to 85	30.2 to 34	15.3 to 19	29.5 to 33

III.3 POROSITY EFFECTS ON ELASTIC PROPERTIES

Young's modulus of Ti-6Al-4V alloys depends on their degree of porosities as well as well as on temperatures and applied pressures. In Ti6Al4V alloys various elastic modulus were obtained by different porosities procedures [3-9]. In the present investigation it is essential to find out relations between the elastic modulus and porosities of Ti-6Al-4V alloys of a density ρ = 4430 g/cm^3. We considered porosities ranging from 61% to 75% as regrouped in Table 3.2.

Table 3.2: Calculated and reported parameters of porous Ti-6Al-4V alloys [1].

Porosity (%)	Experimental			**Calculated**	
	ρ(kg/m^3)	**E(GPa)**	**n**	**B(GPa)**	**G(GPa)**
61	4430	3.8	0.325	4	1.4
62.08		3.55		3.38	1.34
63.3		2		1.86	0.74
65.7		1.1		1.1	0.42
70.6		0.6		0.6	0.23
71.6		0.50		0.5	0.19
75		0.25		0.24	0.09
75.3		0.23		0.22	0.087

III.3.1 Effects of porosity on Young's modulus

It is essential to find out relations between elastic moduli and porosities of Ti-6Al-4V alloys. To describe this dependence, we plot in Fig. 3.1 Young's modulus as a function of porosities for Ti-6Al-4V alloys [1]. It is clear that as the porosity increases, Young's modulus decreases. To quantify this variation, we make use of the approach of curve fitting to find a semi-empirical relation of the form:

$$E\ (\text{GPa}) = 0.28 + 1.43\ 10^{9}\ e^{(-0.32)\ P} \qquad (3.1)$$

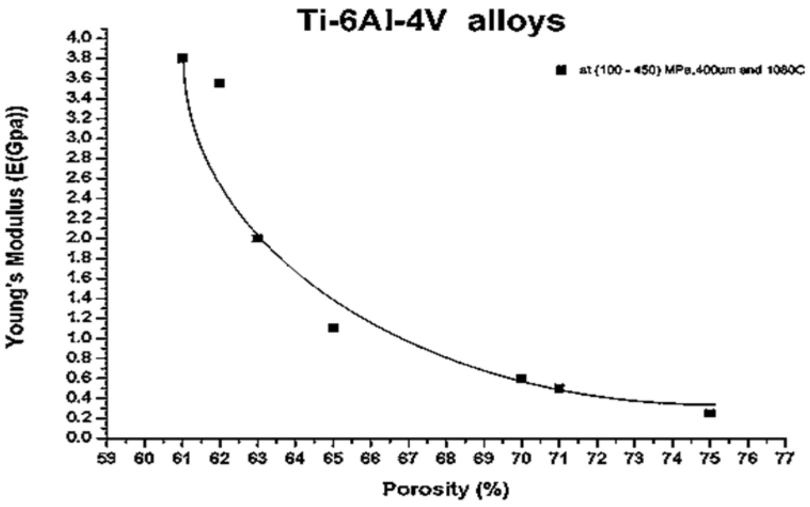

Fig 3.1: Young's modulus of Ti–6Al–4V alloys as a function of porosities.

III.3.2 Effects of porosity on shear and bulk modulus

To enrich the above investigation, it would be essential to find out relations between both shear modulus G and Bulk modulus B as a function of alloy porosities. The obtained results are displayed in fig. 3.2 and 3.3 respectively. It can be seen that as the porosity increases both G and B decrease in a similar way as Young's modulus variations.

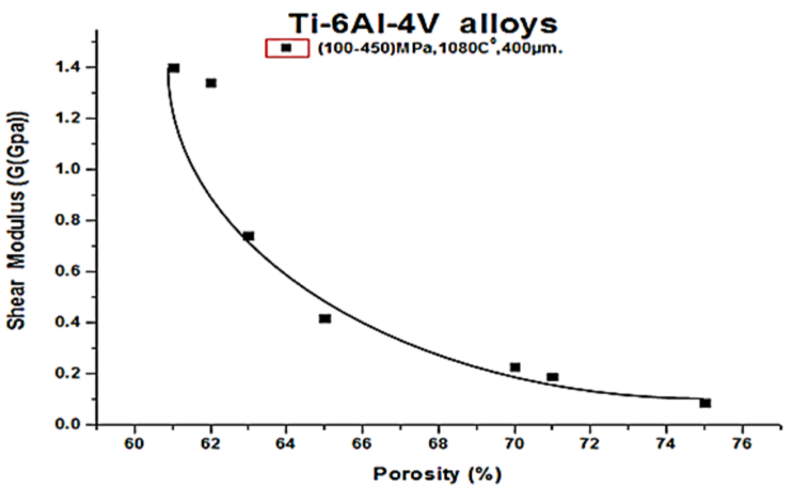

Fig 3.2: Shear modulus of Ti–6Al–4V alloy as a function of porosities.

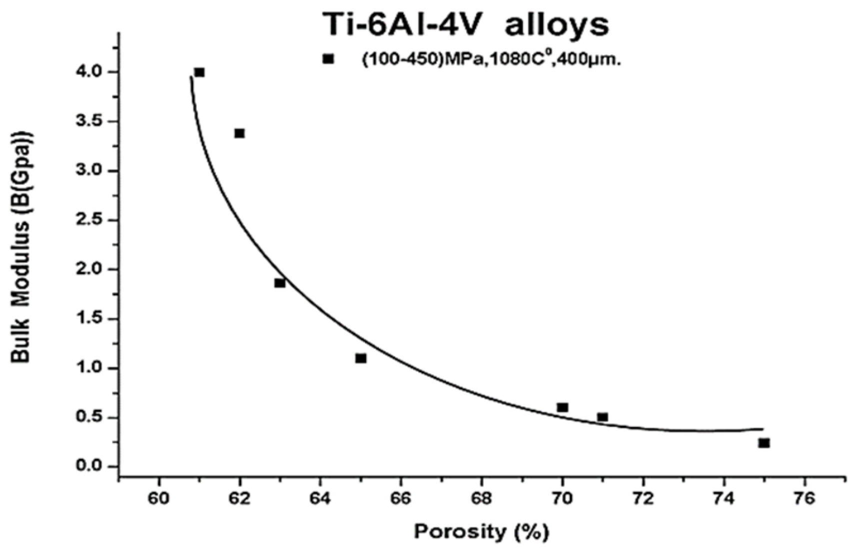

Fig 3.3: Bulk modulus of Ti–6Al–4V alloy as a function of porosities.

The effects of porosity on G and B can be quantified through curve fitting to find the following relations:

$$G = 0.11 + 5.59\ 10^{15}\ e^{(-0.59)\ P} \tag{3.2}$$

$$B = 0.\ 30 + 1.05\ 10^{16}\ e^{(-0.59)\ P} \tag{3.3}$$

It can be concluded that all elastic moduli M (E, G, B) show an exponential decrease with porosities of the form:

$$M\ (GPa) = A + \beta\ e^{-c\ P} \tag{3.4}$$

with A, β and c being characteristic constants typical of different elastic constants as summarized in Table 3.3.

Table 3.3:Characteristic constants in the formula III.4

Elastic Constants	**Characteristic constants**		
	A	β	C
E (GPa)	0.28	$1.43\ 10^{9}$	0.32
G (GPa)	0.11	$5.59\ 10^{15}$	0.59
B (GPa)	0. 3	$1.05\ 10^{16}$	0.59

III.4 POROSITY EFFECTS ON SAW VELOCITIES IN Ti-6Al-4V ALLOYS

Surface acoustic wave velocities properties of isotropic solids may be expressed in terms of independent constants (Young's modulus, *E,* and shear modulus, *G*). Moreover, it is well established that all parameters are related to each other by the following relations [10, 11]:

$$E/G = 2.587 \quad (3.5)$$

$$G = \rho V_T^2 \quad (3.6)$$

$$E = G(3V_L^2 – 4V_T^2)/(V_L^2 – V_T^2) = \rho V_T^2(3V_L^2 – 4V_T^2)/(V_L^2 – V_T^2) \quad (3.7)$$

$$B = \rho\,(V_L^2 - 3/4\ V_T^2) \quad (3.8)$$

$$\upsilon = E/2\,(\rho\, V_T^2) – 1 \quad (3.9)$$

$$V_T = \sqrt{E/2\rho\,(1+\sigma)}. \quad (3.10)$$

$$\sqrt{G/\rho} = VS \quad (3.11)$$

Thus, using relations (3.5 to 3.11), we were able to determine longitudinal and transverse velocities for Ti-6Al-4V alloys at different porosities; the obtained results are regrouped in Table 3.4. To better illustrate the effect of porosities, we plot in Fig 3.4 longitudinal and transverse velocities as a function of various porosity for the Ti–6Al–4V alloys.

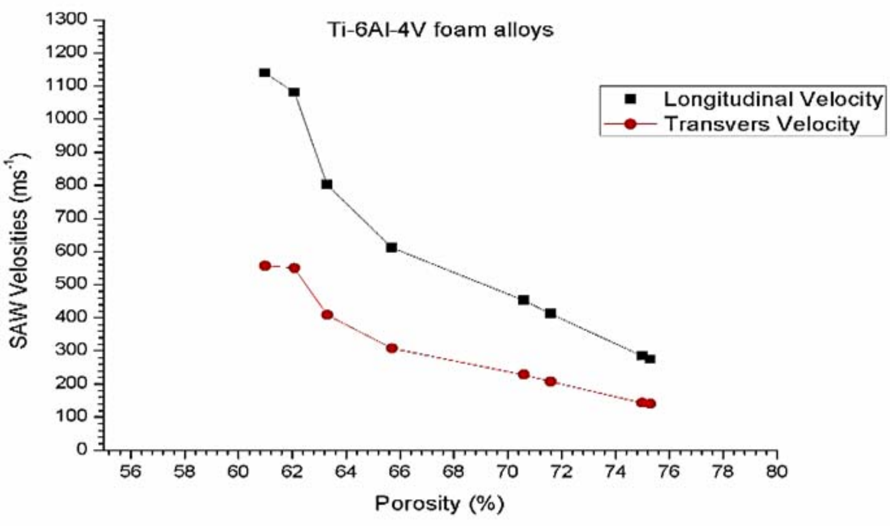

Fig 3.4: Longitudinal and transverse velocities as a function of porosity for Ti–6Al–4V alloys.

It is found that increasing prosperities in Ti–6Al–4V alloys (61% to 75%) leads to a decrease in longitudinal and transverse velocities. In fact, discrepancies in SAW velocities could also be due to different crystal structures (hcp) α-phase and (bcc) β – phase that have been shaped during porosities formation at sintering temperatures and pressures.

Table 3.4: Calculated elastic constants of Ti-6Al -4V alloy with virus porosities.

Porosity (%)	SAW velocity (m/s)	
	Calculated from relations (3.5 to 3.11)	
	V_L (ms^{-1})	V_T (ms^{-1})
61	1139	557
62.08	1080	550
63.3	802	409
65.7	612	308
70.6	452	228
71.6	412	207
75	285	143
75.3	275	140

III.5 EFFECT OF POROSITY ON ACOUSTIC PARAMATERS

Acoustic signatures, or V(z) response, can be either measured experimentally or deduced theoretically. In the present study, as recalled in chapter II, we consider the application of V(z) equations [12-17]. Simulations were carried out in the case of a scanning acoustic microscope at the simulations were carried out in the case of SAM under the following conditions: half lens opening angle θ lens = 50°, a frequency f = 140 MHz and coupling liquids Freon with a density, ρ = 1570 kg/m^{-3} and a velocity, V_{liq} = 716 m/s [15].

III.5.1 Effect of porosity in Ti-6Al-4V alloys on R(θ)

It is more logical to deduce reflection coefficient R(θ) then V(z) curves. The reflection coefficient is a complex-valued function; therefore, we separately calculate its amplitude (modulus) |R (θ)| and phase from equation.

$$R(\theta) = \frac{Z_L \cos^2 2\theta_S + Z_S \sin^2 2\theta_S - Z}{Z_L \cos^2 2\theta_S + Z_S \sin^2 2\theta_S + Z} \tag{3.12}$$

where Z_L, Z_S are the impedance of the two media (liquid and solid). The results thus obtained are illustrated in Fig. 3.5.

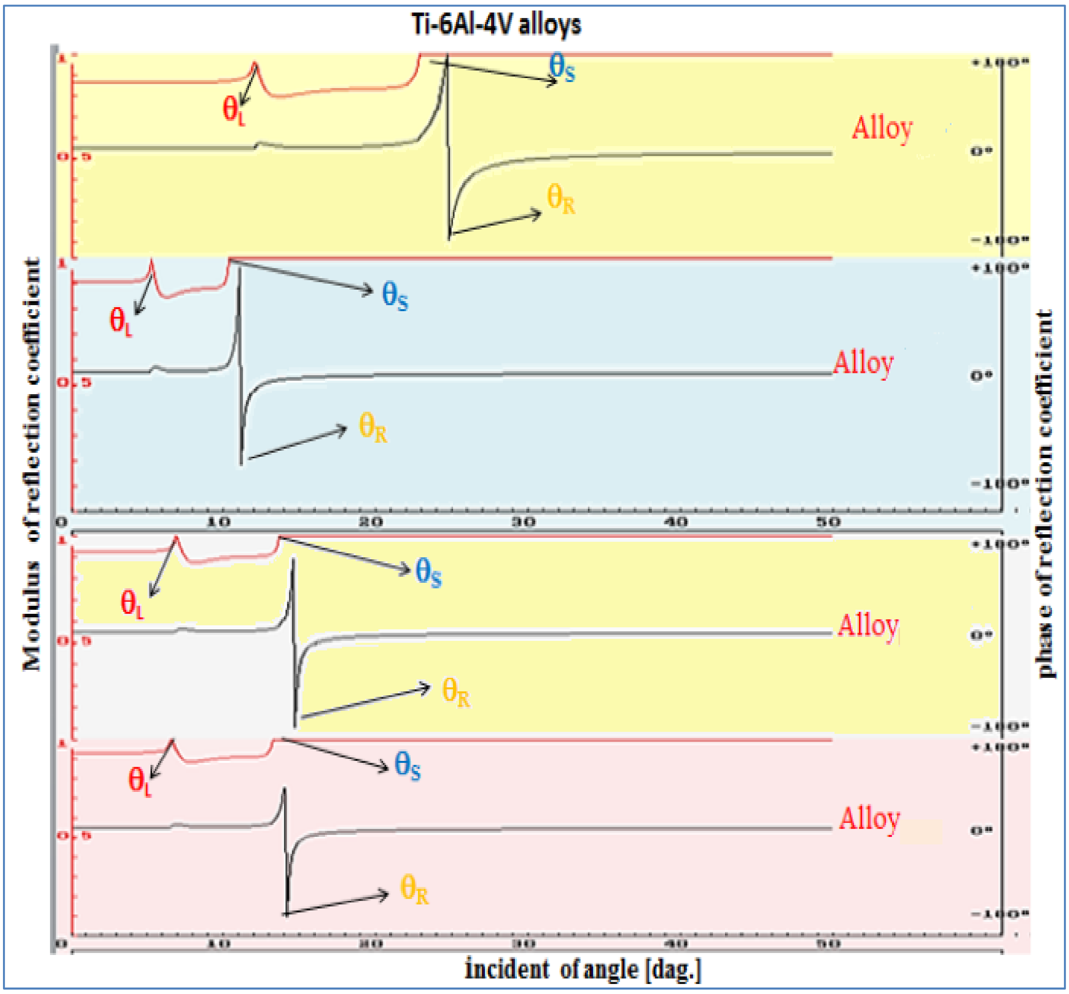

Fig.3.5: Amplitude and phase of reflection coefficient as function of incident angle, modulus and phase of R(θ) as a function of incident angle of Ti6Al4V alloys

It can clearly be noticed that, when the incident angle increases, all the curves exhibit similar behavior: (i) a saturation, (ii) a sharp peak, (iii) another saturation, (iv) a smooth increase and (v) a final saturation with $|R| = 1$. The displacement of all these critical angles is towards lower values (with Freon coupling) when the porosity increases.

(i). The value for zero angle of incidence $\theta = 0$ varied by small amount from porosity. This small variation corresponds to the slight change in the crystal structure due porosity effecting.

(ii). The changes near ($\theta_L = 12.3°; 5.4°; 7.11°$ and $6.8°$) where $|R|$ for all curves first rises to one, which corresponds to the longitudinal-wave critical angle of Ti6Al4V alloys(61%,62%,63%,65% and 70 %) respectively.

(iii). The kink near ($\theta_S = 23.8°; 6.6°; 14.2°$ and $13.3°$) where the value of $|R|$ next rises to one, which corresponds to the shear-wave critical angle for Ti6Al4V alloys (0 %) respectively.

(iv). The constancy near ($\theta_R = 34.5°; 11°; 14.5°$ and $13.5°$) just past the kink, which corresponds to the Rayleigh-wave critical angle for Freon Ti6Al4V alloys (0 %) respectively.

III.5.2 Effect of porosity on V(z) curves and their treatment

Acoustic materials signatures, V(z), curves are calculated for Ti6Al4V alloys at different porosity using previously determined R(θ). Typical results obtained for Ti6Al4V alloys with several porosities are displayed in Fig.3.6 in terms of the output signal, V, as a function of the defocusing distance, z, when the sample is moved vertically in the z axis towards the acoustic lens.

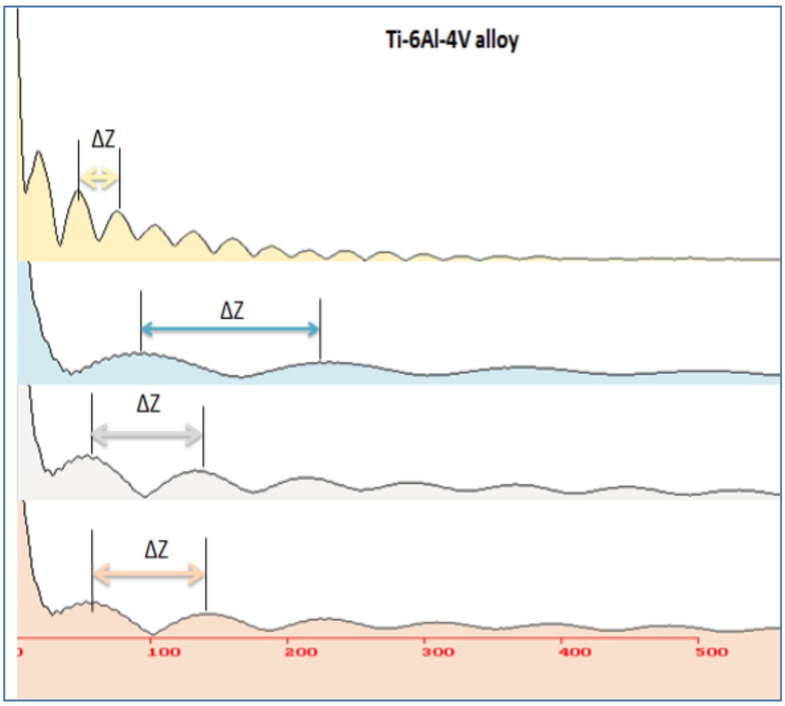

Fig.3.6: V(z) curves of Ti6Al4V alloys at different porosities

It can be seen that there are strong oscillations, where a series of periodic maxima and minima occurs, characterized by a period $\Delta(z)$. This region is characteristic of the sample's acoustic properties. The patterns vary with the material of Ti6Al4V alloys, as do the depths of the minima and the relative magnitude of the maxima which on porosity as well. To analyze and quantify acoustic signature of Fig.3.6, we first subtract the effect of the acoustic lens signal from these curves to obtain the real material signatures as shown in Fig.3.7. Then, these periodic signals can be quantified through fast Fourier transform (FFT), a spectral method used in numerical signal processing.

The deduced FFT spectra, from the acoustic signature of the Ti6Al4V alloys, are displayed in Fig. 3.7.The peak corresponding to the Rayleigh mode appears for all curves

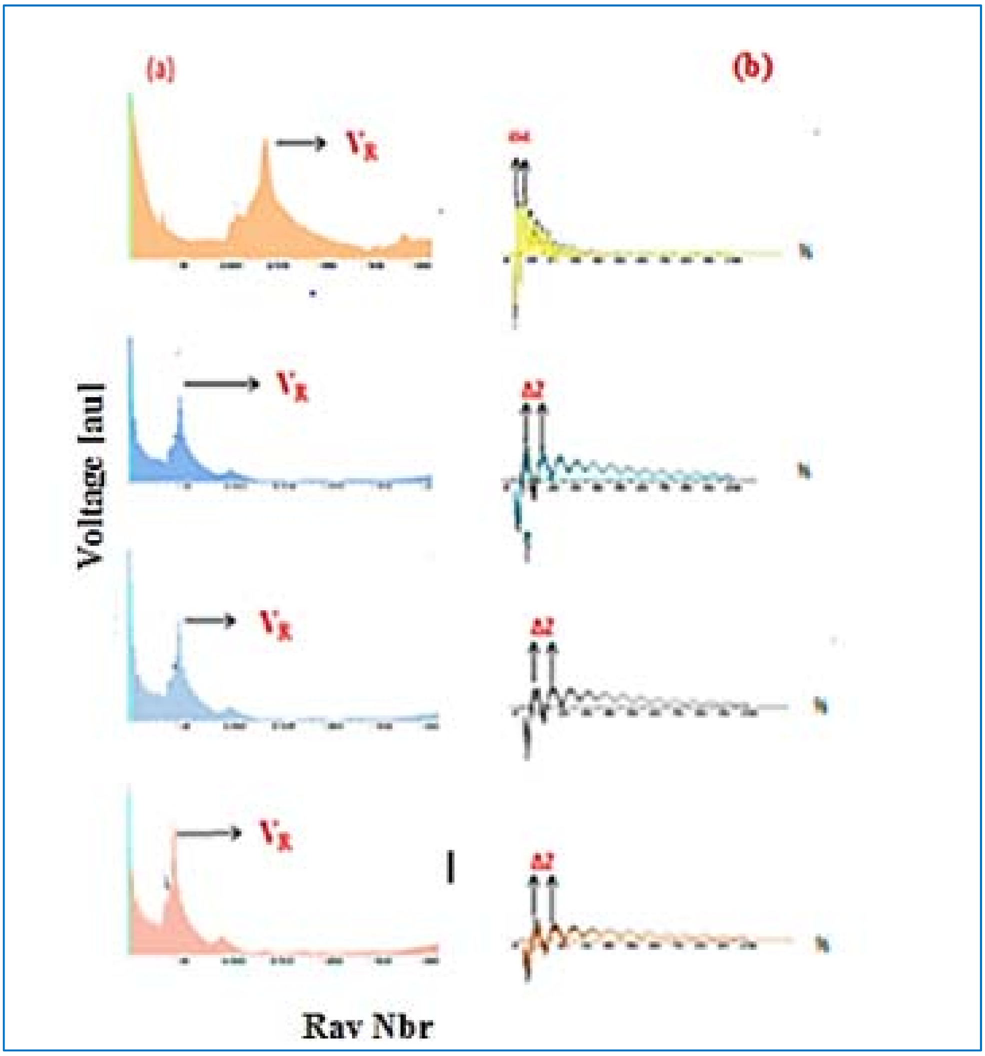

Fig.3.7: FFT spectra and Δz periods of V(z) curves displayed in Fig. 3.6. at different porosities forTi6Al4V alloys

The magnitude of V_R peaks is weakened with increasing the porosity degree. As a consequence, the velocity V_R of the Rayleigh mode is obtained and moved to the lower value of ray number which means that V_R increase with increase porosity. Consequently, each variation in velocities due to shifts in periods) necessarily leads to changes in elastic constants.

III.5.3 Effect of porosity on V_R

To enrich the above investigation on the effects of porosities longitudinal and transverse velocities (§ 4.), we deduced Rayleigh velocities from the SAM simulation of R(θ), V(z) curves and their FFT treatments. From the principal FFT peak, the ryaleigh velocity can be determined from Kushibiki and Chibachi relation [12].

The results thus obtained are tabulated in Table 3.5. It is clear that as the porosity increases, Rayleigh velocity decreases, in agreement with the above behavior of longitudinal and transverse velocities (§ III.4).

Table 3.5: Determined V_R from V(z) curves.

Porosity (%)	V_R (ms^{-1})
61	562
62.08	514
63.3	386
65.7	286
70.6	212
71.6	193
75	136
75.3	98

This dependence is better illustrated in Fig. 3.8 for all SAW velocities (Rayleigh, longitudinal and transverse). The Rayleigh velocity dependence on porosity shows an exponential decay of the form:

$$V_R\,(m/s) = 207.4 + 3.25\ 10^3 \times e^{(-0.41)\,P} \qquad (3.13)$$

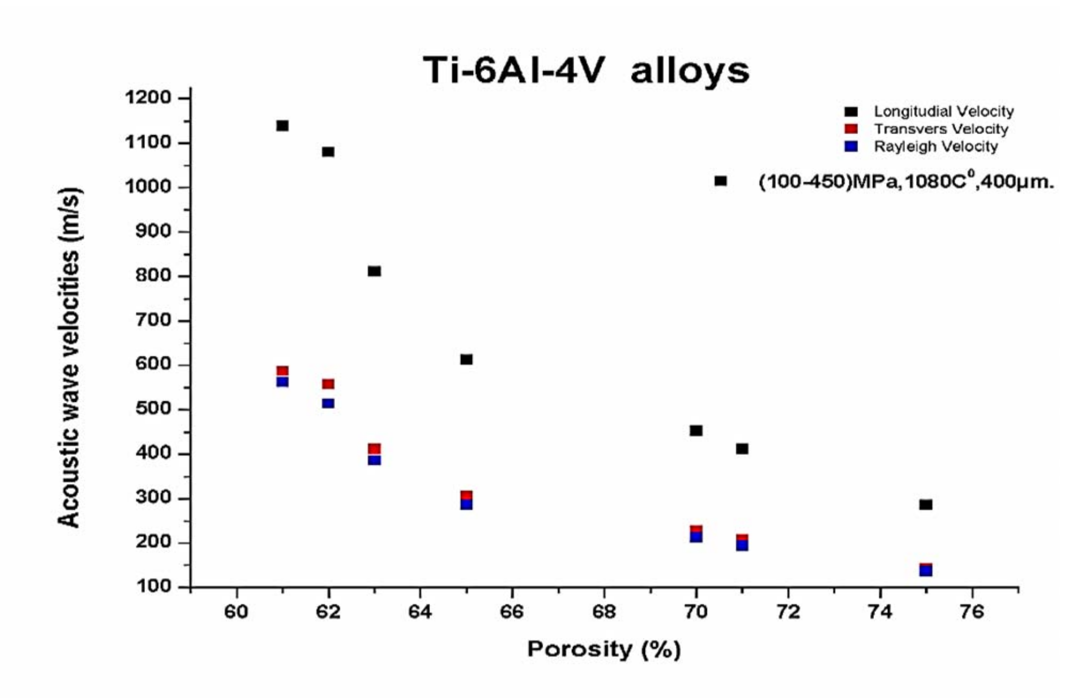

Fig.3.8: Variation of SAW velocities with porosities for Ti6Al–4V alloys

III.6 GENERALIZED POROSITY EFFECTS

The properties of alloys generally depend on the pore characteristics, i.e. type, shape, size, volume percentage, surface area and uniformity of pores, which may be quite different in various production techniques and variable preparation conditions such as pressure and temperature. Therefore, we extend this investigation to all porosity intervals (low, medium and high) of Ti-6Al-4V alloys. Moreover, we consider other parameters such as stiffness coefficients (C_{11}, C_{12} and C44) and acoustic impedance.

The effects of porosities (10% to 75 %) on stiffness constants and acoustic impedances are illustrated in Fig 3.9 and Fig 3.10, respectively. It can clearly be seen that the variations of stiffness constants and acoustic impedances with porosities follow a general trend consisting of a decrease with increasing porosities, as deduced earlier in previous paragraphs.

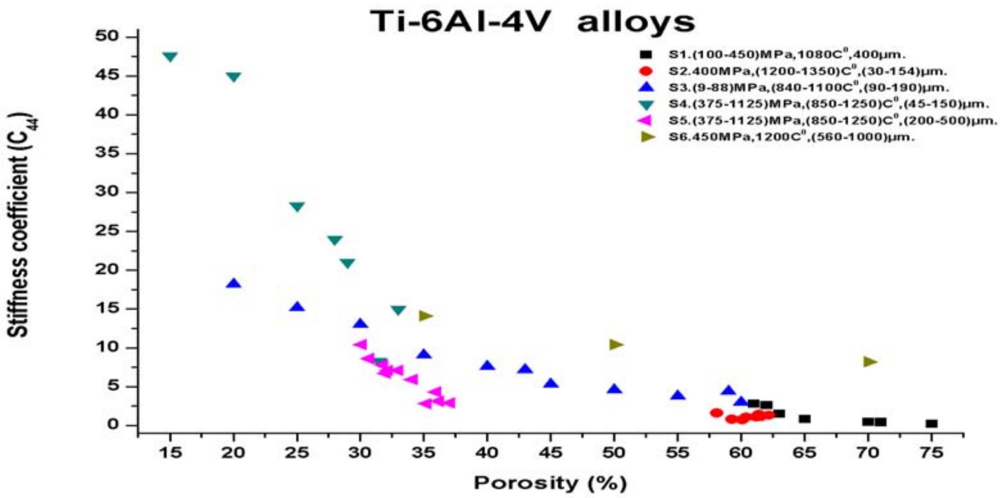

Fig 3.9: Porosity effects on stiffness coefficients (C11, C_{12} and C44) for the Ti–6Al–4V alloys.

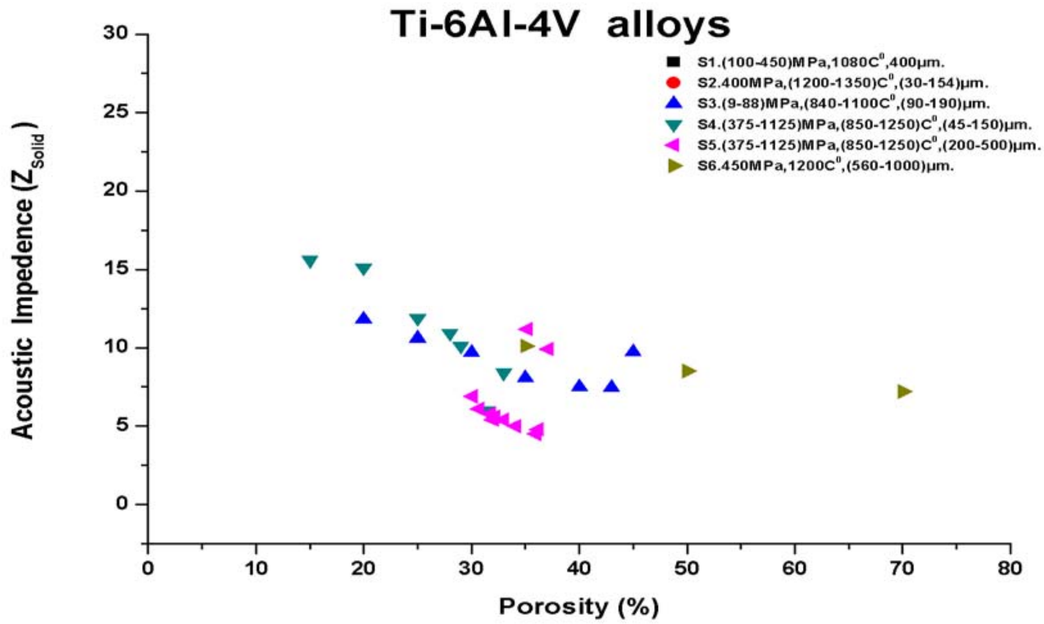

Fig 3.10: Porosity effects on acoustic impedance for the Ti–6Al–4V alloys.

III.7 APPLICABILITY OF Ti-6Al-4V ALLOYS AS HUMAN BONES

It is worth noting that human bones are characterized by elastic moduli values ranging from 0.1 to 40 GPa. Therefore, it would be interesting to find implants with similar mechanical characteristics. In this context, elastic modulus of titanium and titanium alloys depend on their degree of porosities: it changes from 3.8 to 0.23 GPa (Table 3.2) when porosities vary from 61% to 75 %. Therefore, Ti-6Al-4V alloys seem to be the best candidates to replace human bones, as implants. It should be noted that all other elastic parameters follow the same behavior, i.e., the deduced changes for shear modulus, bulk modulus, longitudinal velocities, shear velocities, Rayleigh velocities and stiffness coefficients (C_{11},C_{12} and C_{44}) vary from, (4 to 0.24) GPa, (1.4 to 0.09) GPa,(1139 to 285) m/s, (587 to 143) m/s, (562 to 136) m/s, (501 to 421) m/s, (7.7 to 0.5) GPa, (4.9 to 0.3) GPa and (2.8 to 0.2) GPa, respectively.

Therefore, according to their porosities, Ti–6Al–4V alloys can be used as implants in human bodies to replace different human bones (cortical, trabecular, concelleus) as summarized in Tables 3.6 and 3.7 that regroup elastic constants and surface acoustic wave velocities.

Table 3.6: Elastic properties of Ti–6Al–4V alloys with different porosities

Bones	Porosity(%)	Elastic modulus (GPa)		
		E	G	B
Cortical	28 to 37	10 to 20	3 to 7.5	10 to 23
Trabecular	57 to 64	2.5 to 7.5	0.5 to 3	2 to 8
Cancellous	60 to 75	0.05to1.95	0.09 to 1.3	0.1 to 1.5

Table 3.7: SAW velocities of Ti–6Al–4V alloys with different porosities.

Bones	Porosity(%)	SAW velocities		
		V_L	V_T	V_R
Cortical	30 to 44	1500 to 2800	750 to1500	700 to 1250
Trabecular	58 to 65	700 to 1500	350 to 700	300 to 700
Cancellous	60 to 75	1139 to 285	557 to143	562 to 130

For clarity, we plot in Fig. 3.11 (a) and (b) the most accurate intervals of porous Ti–6Al–4V alloys which gives the closest values to realistic and conformity to elastic modulus and acoustic wave velocities of (cortical, trabecular and concelleus) bones.

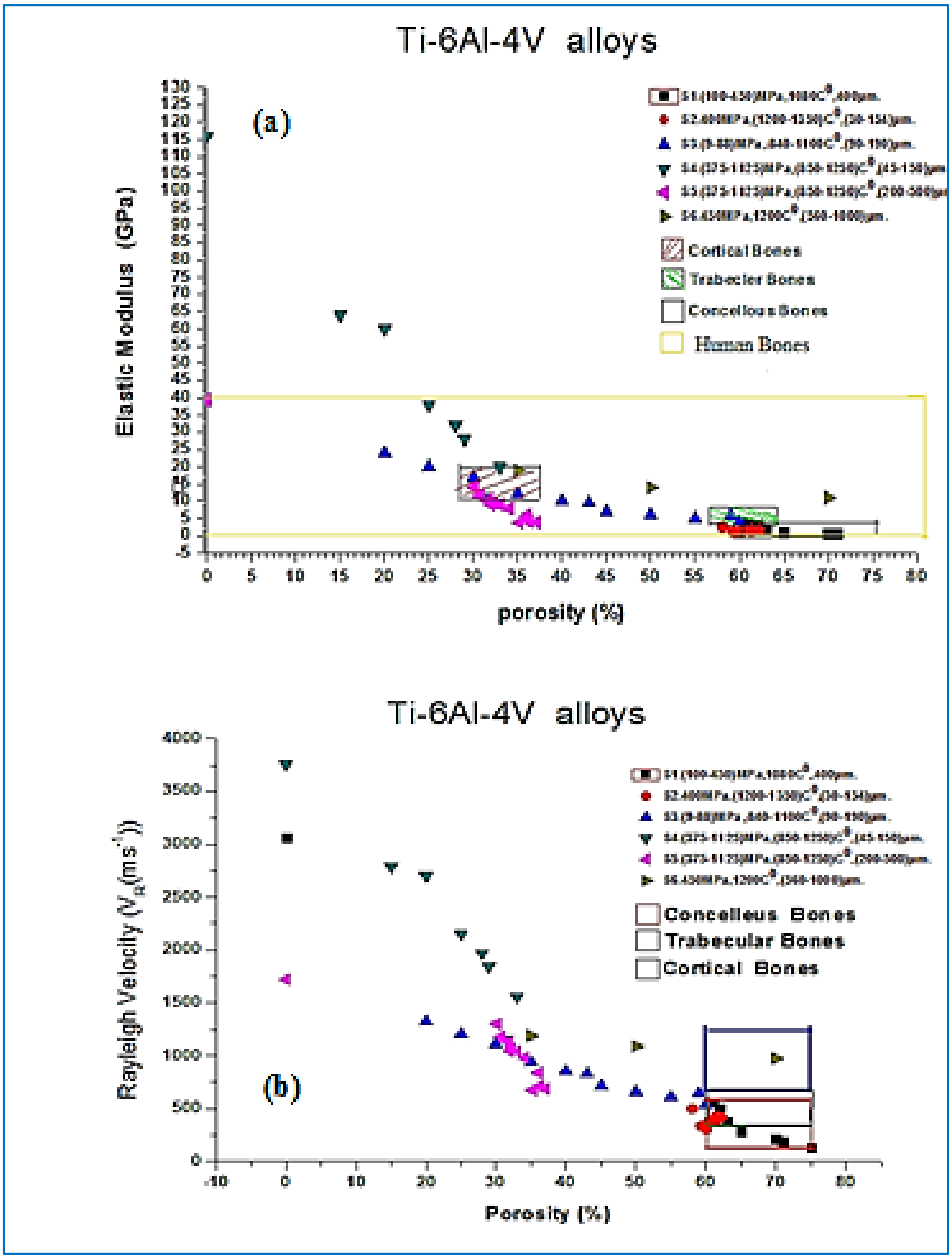

Fig. 3.11: Porosity effects on elastic modulus (a) and Rayleigh velocity (b) Ti–6Al–4Valloys with porosity, together with applied intervals to cortical, trabecular and cancellous bones.

III.8 EFFECTS OF BORON ADDITION TO Ti–6Al–4V ALLOYS

III.8.1 Effects on elastic moduli

Ti–6Al–4V alloys are mainly used for replacing materials for more Application. Alloys cracks are, therefore, one of the big problems for their unfailing use in the body. The crack appearances of the alloys are affected by changes in microstructure. The effect of addition of Boron on Ti–6Al–4V alloys of the mechanical properties is also very important to understand the effects of simulated to changes of elastic modules to calculating of the acoustic materials signature curves. Whoever, body environment to the moduli of elasticity of biomedical titanium alloys on the mechanical properties [21]. Elastic properties of objects are very major, since their measurement gives evidence about the forces that are performing between the fundamental atoms of materials. This is of unlimited importance in understanding to properties of bonding in the materials. It has been found that minor addition of B (up to 0.1 wt %) to Ti64 reduces the grain size dramatically (by more than an order of magnitude) and increases the tensile properties such as yield and ultimate tensile strengths [22].

The effect of minor amount of B addition on elastic modulus (E) of Ti64 has not yet been examined in detail, which is the objective of this work. Different alloys of Ti–6Al–4V–xB (with x = 0.0, 0.04, 0.09, 0.30 and 0.55 wt % B1) were reported [22, 23] and investigated in this work (Table 3.7).

Table 3.8: Elastic moduli of Ti–6Al–4V alloys with boron element addition [22, 23]

Boron addition Ti–6Al–4Valloy	**Experimental**	**Calculated**	
	E(GPa)	**B(GPa)**	**G(GPa)**
0.0	113	110.8	42.5
0.04	121	118.6	45.5
0.09	114	111.8	42.8
0.3	120	117.7	45.1
0.55	126	123.5	47.4

The effects of Boron addition to Ti–6Al–4V/xB alloys on elastic modulii on Young's modulus, shear modulus, and bulk modulus at different additional Boron are shown in Fig.3.12**.** A slight increase is obtained for all mechanical constants (E, G, B,) for porosities higher that 10%.

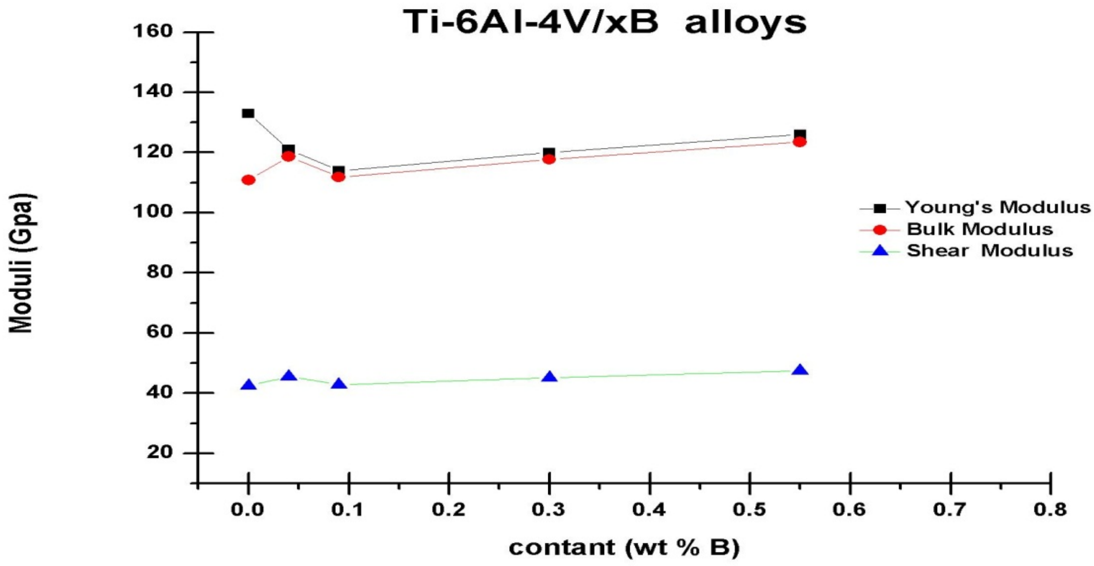

Fig.3.12: Effects of B addition to Ti–6Al–4V/xB alloys on elastic moduli

III.8.2 Effects on acoustic parameters

To investigate the effects of boron addition on acoustic parameters (SAW velocities), we calculated V(z) curves, their periods and finally the corresponding velocities. The obtained results are plotted in Fig. 3.12. It is clear that the periods Δz in V(z) curves depend on the amount of B additions and consequently the values of SAW velocities. The obtained results are regrouped in Table 3.8.

The curves in Fig. 3.13 confirm that the velocities increase with xB**.** In fact, it was found that as xB change from 0.0 wt.% B to 0.55 wt.% B. V_L increases from 6148m/s to 6492m/s, V_T from 3097m/s to 3171m/s and V_R from 2864m/s to 2927m/s. Moreover, a change of xB from 0.0 wt.% B V_L increases Δz from 79.4 to 83 All these observations are regrouped in Table 3.9**.**

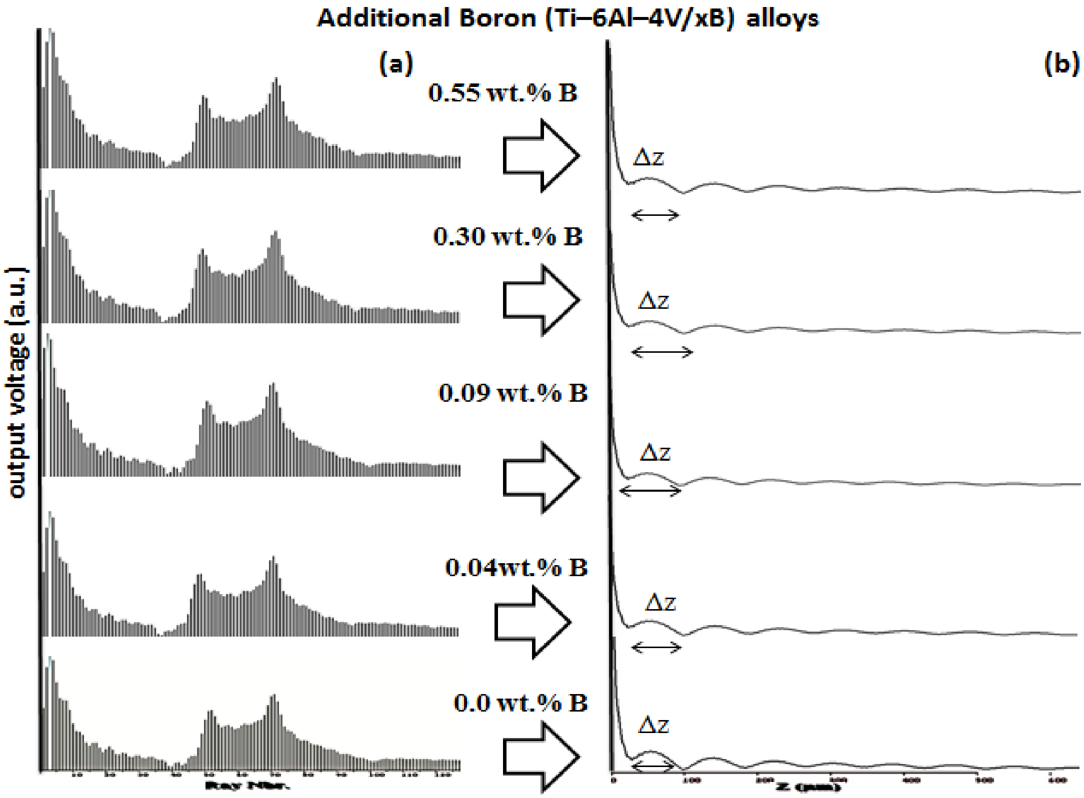

Fig.3.13: Acoustic materials signatures and their FFT spectra of several xB additions (0.0 < x ≤ 0.5) wt.% B of Ti–6Al–4V alloys.

*Table 3.9**:** Characteristic acoustic parameters of several xB addition (0.0 < x ≤ 0.5) wt.% B of Ti–6Al–4V alloys.*

B addition in Ti–6Al–4Valloys	acoustic periods	(SAW) velocities		
wt.% B	**Δz(μm)**	**V_L (m/s)**	**V_T (m/s)**	**V_R (m/s)**
0.0	79.4	6148	3097	2864
0.04	84.3	6361	3205	2951
0.09	80.5	6174	3108	2884
0.3	84	6336	3191	2944
0.55	83	6492	3171	2927

III.9 CONCLUSIONS

In this chapter, we investigated several Ti-6Al-4V alloys that can be used as implants to replace different types of human bones. These alloys are characterized by their porous character. Therefore, the porosity effects on mechanical constants (E, G, B, C11, C12, C44) as well as acoustic parameters (R(θ), V(z), V_L, V_T, V_R, Z) have been investigated.

These effects were quantified and relations were deduced in all cases. They show an exponential decay with increasing porosities. The importance of establishing such formula lies in their applicability to the prediction of the exact porosity for a given parameter and vice versa. Consequently, this allows the preparation of the required alloys for the replacement of a given bone types (cortical, trabecular and cancellous bones). Moreover, the effects of boron addition to Ti-6Al-4V alloys on acoustic parameters (SAW velocities) have also been investigated; such additions improve the quality of the material.

GENERAL CONCLUSIONS

Ti-6Al-4V alloys with several porosities (61% to 75%) are investigated. This work concerned the porosity effects, P, on different elastic constants and acoustic parameters elastic: Young's modulus E, shear modulus G, Bulk modulus B, Poisson coefficient σ , longitudinal velocities, shear velocities and Rayleigh velocities and modulus of elasticity, stiffness coefficients (C_{11},C_{12} and C_{44}) and acoustic impedances.

It is found that the general trend of porosity-parameter variations is characterized by a decrease of all investigated elastic and acoustic parameters as the porosity increases. The quantification of this behavior led to the determination of analytical relations which were expressed as:

For elastic moduli, M (E, G, B), the dependence takes the form:

$M = A + \beta\, e^{-c\, P\,(\%)}$ with A, β and c being characteristic constants.

Whereas, for SAW velocities (V_L, V_T, V_R), it is found that: $V = A' + \beta'\, e^{c' P(\%)}$.

The importance of establishing such formula lies in their applicability to the prediction of the exact porosity for a given parameter and vice versa. Consequently, this allows the preparation of the required alloys for the replacement of a given bone types.

Moreover, the effects of boron addition to Ti-6Al-4V alloys on SAW velocities have also been investigated; such additions improve the quality of the material.

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