

## *Chapter 2*

### *Literature Survey*

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#### **2.1 Introduction**

The present chapter is a detailed review of research works reported in the literature related to the Titanium, their alloys and bioactive glasses used in biomedical application. Their attractive and excellent properties make it a suitable candidate to be used as composite materials. This brief literature review helped the accomplishment and planning of the research work for synthesizing of desired composites and its recent applications.

The need of implant and bone replacement has not been restricted up to only aged people. The metal biomaterials have been used widely in medical implants because of the adequate formability, strength and fracture resistance. It is estimated that 65%–85% of implants materials are consists of metallic materials. Metallic implants are considerably important for the rebuilding of damaged hard tissue and it has been observed that the growth rate of these implant market remains at around 20% and 25%. [1].

The biocompatibility of implant materials is of prime interest because they can corrode in the hostile body environment [3]. Most metals which are used in the implants (e.g., Fe, Cr, Co, Ni, Ti, Ta,Mo, and W) can be accepted by the human body in very little amounts. these type of metallic materials, in naturally forms, are crucial in the many rolls like functioning of cell (Fe), synthesis of a vitamin B12 (Co), and crosslinking of elastin in the aorta (Cu) but cannot be accepted in large amounts in the body. “Vanadium steel was the first medical alloy which is developed for human and was

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used to manufacture bone fracture plates which are called Sherman plates and screws. But was not be in use in implants due to its corrosive nature in vivo environment [4, 5]. Later, 18-8 steel having low carbon and Molybdenum which is known as 316L stainless steel was came into existence and currently is used for implant manufacture. This alloy shows comparably good resistance of corrosion to chloride and weak sensitization [6, 7]. The CoCrMo alloy has also been used for many decades in implantation and recently, in making artificial joints [8].

## **2.2 LITRETURE SURVEY**

Amid all domains of metallic biocompatible materials, commercial titanium (C.P. Ti) and their alloy have gained good courtesy in the biomedical field because of their biological compatibility and considerable large resistance of corrosion. The corrosion protection is due to the formation of a shielding and firm layer of oxide on the metallic implant surface. [9, 10]. In the late 1930's, the attempt had been began to use it as implant, as it was found compatible in cat femur.

About 0.6%. of Titanium is found in the earth's crust but Unfortunately, it is rarely found in high quantity and occurs with impure state. Titanium's lightness and good mechano-chemical properties are the key properties for implant application. These materials are known as biologically inert biomaterials because they remain basically unaffected upon implanted in human bodies. The human body identifies these materials as foreign materials and therefore forces to detach them by making encapsulate it in fibrous tissues [11, 12]. It has very low density as compared to the other bio implant metals being  $4.5 \text{ gm/cm}^3$

It is observed that the titanium has same level of compatibility within the body as steel and cobalt are having. Ti is naturally biocompatible and often shows direct bone apposition. The magnetic susceptibilities of Ti and Ti-6Al-4V alloy are is  $31.9 \times 10^{-9}$

$\text{m}^3 \text{kg}^{-1}$  and  $39.8 \times 10^{-9} \text{ m}^3 \text{kg}^{-1}$  respectively which are less than that of Co–Cr–Mo alloy i.e.  $94.5 \times 10^{-9} \text{ m}^3 \text{kg}^{-1}$ , and stainless steels, avoiding the influences of magnetic resonance imaging (MRI), such as motion, attraction force, torque, heat generation, and artifacts [13, 14, 15]. This property is very much significant, since magnetic resonance imaging is most often being used for medical examination.

The first boom on the status of commercially pure Ti for the use of medicine was seemed in 1940, which showed the good compatibility with bone based on an animal test [16]. So, the compatibility to bone and soft tissue of rabbits [17], its non-cytotoxicity due to good resistance of corrosion in body surroundings [18], and brilliant biocompatibility in dogs were stated. The industrial manufacturing in large scale for Ti has been achieved in the late 1940s made it conceivable to carry out many research finding for medical applications, enlightening great biocompatibility in long-term animal testing [19]. Hence, the fruitful application of CP Ti was broadly documented by the last half 1960s through clinical evaluation [20, 21].

Commercially pure Ti alloys are also being used for bone plates, especially curved ones, where grades 1–4 can be taken depending on the strength of alloy. CP Ti is categorized into four grades which have slight difference in the oxygen moiety. The oxygen content of Grade 4 is maximum i.e. (0.4%) and grade 1 possess the minimum (0.18%) oxygen. [22]. These different grades are having different mechanical properties due to the impurities that are present in small amount. For improving corrosion resistance, iron is mixed and to enhance the strength and decreased density Al is added, while vanadium acts as an aluminum scavenger to prevent corrosion [23, 24]. Dental and orthopedics implants, artificial hearts, pacemakers, artificial knee joints, bone plates, cardiac valve prostheses, screws for fracture fixation, artificial hip joints are few areas where Ti is used [25].

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The CP-Ti is synthesized via the conventional routes i.e. strips, sheets, plates, bars, billets, forgings and wires are specified according to the American Society for Testing and Materials (ASTM) as grades 1 to 4. Table summarizes the mechanical properties of titanium according to the ASTM standards F67 [26] and F136 [27] for bars, billets and forgings. Grade 2 titanium is the main unalloyed Ti used in dental implant applications. Grade 2 Ti has minimum yield strength of 275 MPa and this is the equivalent of yield strength in heat-treated austenitic stainless steels [28]

**Table 2.1** Chemical Compositions of Pure Titanium (F67; ASTM, 2000)

Element	Grade 1	Grade 2	Grade 3	Grade 4
N	0.03	0.03	0.05	0.05
C	0.10	0.10	0.10	0.10
H	0.015	0.015	0.015	0.015
Fe	0.20	0.30	0.30	0.50
O	0.18	0.25	0.35	0.40
Ti		Balance		

**Table 2.2** Chemical Compositions of Pure Titanium

Material Specification	Tensile Strength	0.2% stress	Proof	Elongation	Elastic Mod
ASTM F67 Grade 1	240	170		24	103–107
ASTM F67 Grade 2	345	275		20	103–107
ASTM F67 Grade 3	450	380		18	103–107
ASTM F67 Grade 4	550	483		15	103–107
ASTM F136 Grade 5	860	795		10	114–120

Although titanium shows better corrosion resistance and tissue compatibility than stainless steels and Cr- Co-based alloys, yet it's some mechanical properties and tri-biological performance confined it to be used as biomaterial in some of the cases. This is mainly true where high mechanical strength is required and the strength of cp Ti remains below the normal thresholds value, like in hard tissue replacement or in the case where highly intensive wear occurs. Infact, the need for greater strength has led to the increasing use of grade 4 commercial purity titanium for bio devices, the mechanical strength rises above that of grade second which is being obtained through an increment of the oxygen motility [29].

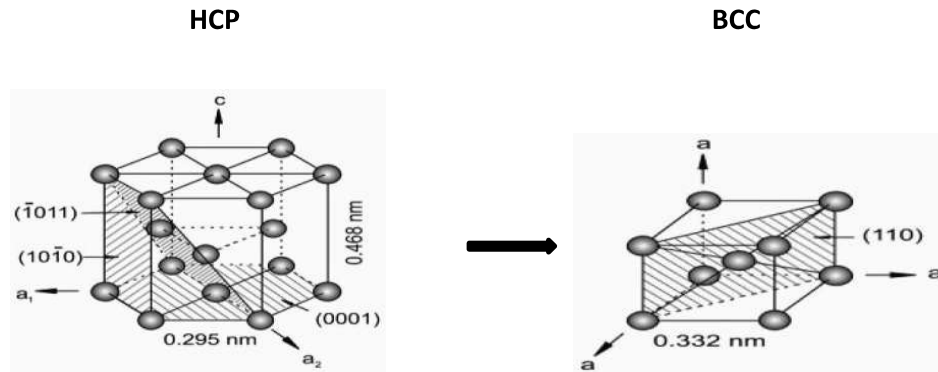
To overcome such drawbacks, commercial pure titanium was replaced with titanium alloys which may have some improved mechanical properties. One of the important aspect is the growth of fibrous connective tissue on the surface of the implant in order to avoid the complications. The interfere of fibrosis occurs with curing of the damage created during implant surgery [30]. In that context, Ti alloys is found to produce very little fibrous tissue as compared to Cp Ti and therefore bone can nurture very easily. The mechanical properties of these Ti alloys can be improved through different phase structure by alloying different type of alloying components.

### **2.2.1 Crystal structure and phase stability of titanium and its alloys**

At  $882\pm 2$  °C, Titanium shows an allotropic transformation from the alpha (HCP) phase to the high temperature beta (BCC) phase. Figure 2.1 shows  $\alpha$  to  $\beta$  phase transformation. The temperature at which beta to alpha transformation occurs is called the  $\beta$ -transus and depends on the amount and type of alloying elements added [31]. The alloying elements that are dissolved in titanium may stabilize  $\alpha$  or  $\beta$  phase. Titanium and its alloys react with interstitial elements such as oxygen, nitrogen, and hydrogen, below their respective melting points. In this, titanium produces solid

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solutions and compounds having metallic, covalent or ionic bonding on reacting with other elements. The alloying elements which are added to improve mechanical properties and corrosion resistance are classified as  $\alpha$ -stabilizer, or  $\beta$ -stabilizers



**Fig. 2.1** Crystal structure of  $\alpha$  (HCP) and  $\beta$  (BCC) phase [31].

So the alloying elements are classified into three classes as  $\alpha$ -stabilizer,  $\beta$ -stabilizer and neutral. The  $\alpha$ -stabilizing elements stabilize the alpha phase field to higher temperatures, on the other hand,  $\beta$ -stabilizing elements are those which extend the beta phase to low temperatures. Neutral elements either zero or little influence on the  $\beta$  transition temperature [32].

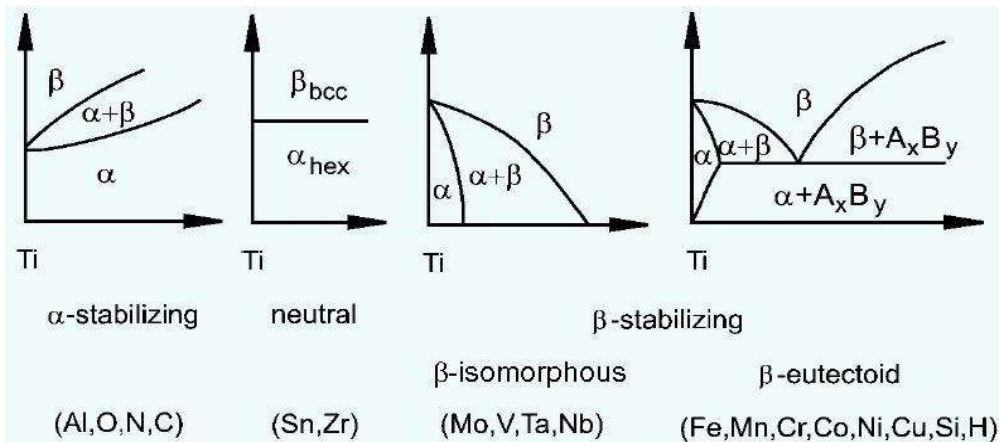
### 2.2.2 Alpha ( $\alpha$ ) Stabilizers

Main  $\alpha$ -stabilizing elements are Al, Sn, O and N which improve the solid solution strengthening and corrosion resistance. Among above, aluminum is the widely used and significant alloying element. Al is the principle alloying element because it is one of the strongest  $\alpha$  stabilizers. Al is a very active alpha-stabilizing element at temperatures up to about 550 °C. The low density of aluminum is an important feature but the amount of aluminum is limited due to the formation of a titanium aluminium compound of brittle nature,  $Ti_3Al$ , at aluminum contents exceeding about 8wt. %. Sn also plays the role of  $\alpha$  phase stabilizer to improve ductility [33]. Oxygen and nitrogen

are normally present as impurities and contribute to interstitial hardening. A small amount of oxygen is used to provide a specific range of strength levels in several grades. These alloying elements tend to increase the strength but decrease the ductility of Ti alloys [34].

### 2.2.3 Beta ( $\beta$ ) Stabilizers

Those elements which reduce the transformation temperature ( $\alpha/\beta$ ), fortify the beta phase and exhibit low solubility of alpha phase termed as  $\beta$ -stabilizers. They are of two types;  $\beta$  isomorphous elements, and  $\beta$  eutectoid elements resulting from the binary phase diagrams. The phase diagrams are shown schematically in Fig. 2.2.  $\beta$  isomorphous elements used in titanium alloys are Ta, V, Mo, and Nb. Of these, the  $\beta$  isomorphous elements, e.g. Mo, V, and Ta, are by far more important due to their much higher solubility in titanium. They have complete solid solubility in  $\beta$  titanium. Adequate amount of these essentials make it promising to alleviate the  $\beta$  phase to room temperature [34]. Other elements related to this domain that are not used at all due to point of view of density, are Ta and Re.



**Fig 2.2 alpha and beta stabilization of Titanium**

On the other hand, the  $\beta$  eutectoid stabilizers which are generally used for alloying with Ti are Cr, Fe, Mn and Si and can lead to the formation of intermetallic compounds, while Padanium, Nickel, Copper, tungsten, and Bismuth have only inadequate usage [34]. There are other beta eutectoid forming elements, like Cobalt, silver, Gold, Platinum, Beryllium, lead, and Uranium, are not cast-off at all in titanium alloys [36].

Although the hydrogen is also belongs to these  $\beta$  eutectoid forming elements and the low eutectoid temperature of 300°C along with the high diffusive property of hydrogen led to a special kind of refinement of microstructure, and so-called hydrogenation/dehydrogenation (HDH) process. Offenly, the content of hydrogen in CP titanium and titanium alloys is sharply limited to around 125-150 ppm due to hydrogen embrittlement [37].

#### ***2.2.4 Neutral Elements***

Zirconium and Halfminium are reflected as neutral elements because they decreases the  $\alpha/\beta$  transformation temperature very slightly and then raises the transformation temperature again at higher side of concentrations. Both exhibit the same beta to alpha allotropic phase transformation and are isomorphous with both the phases of titanium. Tin also has very slight effect on the  $\alpha/\beta$  phase boundary. But if we consider in strength; they are not be consider as a neutral because they mostly strengthen the phases [38].

### **2.3 CLASSIFICATION OF TITANIUM ALLOYS**

(Surgical tool) Ti can have two different types of basic crystal structures. At elevated temperatures, Ti has a very stable bcc phase known as  $\beta$ -Ti on the other hand, at the transus temperature ,it experiences an allotropic modification where beta titanium

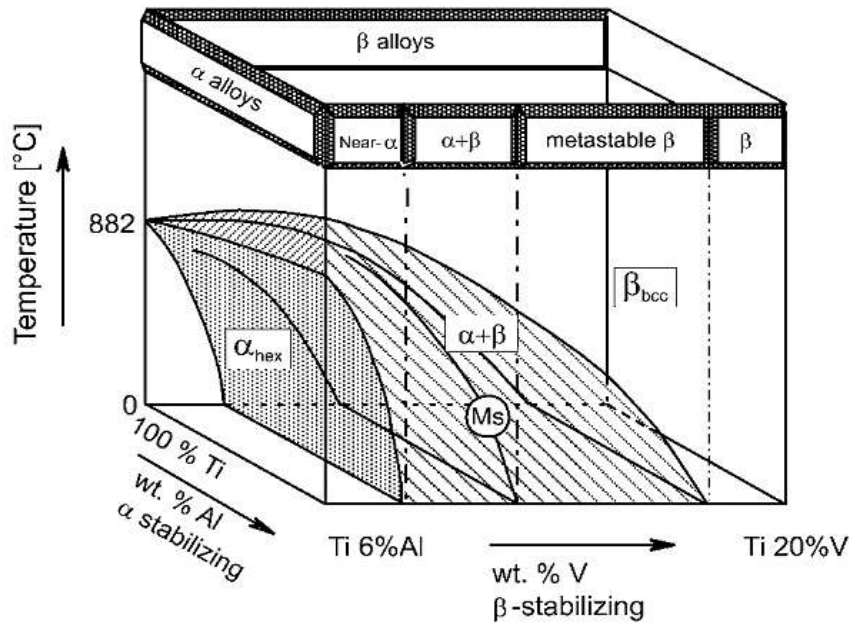
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changes from bcc to hexagonal close packed (hcp) structure, termed as a alpha-Ti, which is established at lower temperatures. Because of rearrangement of these two crystal structures, we get the broad range of properties of Ti alloys that impacts both plastic deformation and rate of diffusion.

Based on the phases present at room temperature, titanium alloys are categorized into four groups

- a)  $\alpha$  alloys (commercially pure titanium)
- b) Near  $\alpha$  alloys,
- c)  $\beta$  alloys, and
- d)  $\alpha+\beta$  alloys.

Figure 2.3 schematically represent the phase diagram; this three dimensional diagram has two phase diagrams with alpha and beta stabilizing elements. According to this diagram, alpha alloys consists of alpha phase and are completely alloyed with  $\alpha$  stabilizing elements. If little quantity of  $\beta$  stabilizing elements is added, they are termed as near  $\alpha$  alloy. The  $\alpha+\beta$  alloys are the frequently used titanium alloys [39 Evans (1998)]. These alloys have  $\beta$  volume fraction ranging from about 5 to 40% at room temperature. If the percentage of  $\beta$ -stabilizing elements is again changing to a level where beta is no longer transforms to martensite in quenching, the alloys are still in the double-phase and the metastable state of beta alloys will be achieved. Remarkably these alloys can still able to produce an equilibrium volume fraction of more than 50% of beta. Finally, the single-phase  $\beta$  alloys mark the end of the alloying scale of the conventional titanium alloys [35].



**Fig. 2.3** Schematic phase diagram of titanium alloys [31].

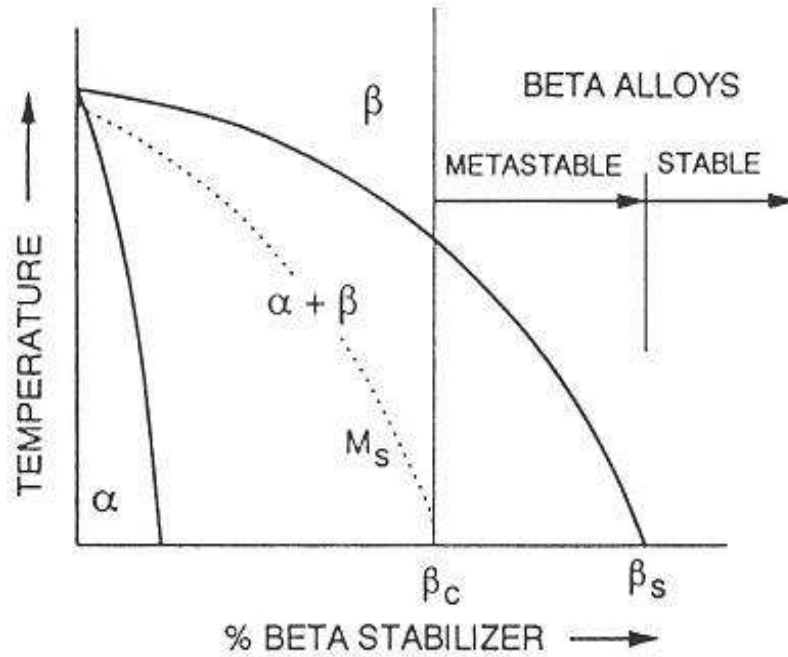
Alpha is the low-temperature allotrope of titanium, and the microstructure of  $\alpha$  alloy consists predominantly of the  $\alpha$ -phase. They are used as airframes, heat exchangers due to their considerable large creep resistance and corrosion resistance. They are also used in medical devices because of their corrosion resistance.  $\alpha$  alloys are the most weldable and non-heat treatable titanium alloys. They are also used largely in cryogenic applications at  $-253\text{ }^{\circ}\text{C}$ . Their properties are strongly dependent on texture [34]. The typical applications and tensile strength of  $\alpha$  alloy are recorded in Table 2.3

Near- $\alpha$  alloys contain a small amount of  $\beta$  stabilizers like Mo and V which provide a microstructure of  $\beta$  phase dispersed in the  $\alpha$  phase structure. They are cast-off in gas turbine engines of aircraft components like compressor disc at high temperatures up to  $550^{\circ}\text{C}$ .

S. No.	Grade	wt.%	Tensile strength	
			YS (MPa)	UTS (MPa)
1.	High purity	99.98	140	235
2.	1	99.5	170-310	>240
3.	2	99.2	>310	390-540
4.	3	99.1	350-450	550-600
5.	4	99.0	480-655	>550

**Table 2.3 Typical applications and tensile strength of different grades of  $\alpha$  alloys**

A compressor disc made of near- $\alpha$  alloy Ti-6Al-5Zr-0.5Mo-0.25Si (IMI 685) is shown in Fig. 2.4. The presence of the  $\beta$  phase permits two-phase strengthening through control over the scale, morphology and distribution of the two phases [40]. The mechanical properties of near  $\alpha$  alloys are superior to those of  $\alpha$ -alloys, further, due to the presence of  $\beta$  phase, these alloys are heat treatable. They possess higher strength than those of  $\alpha$  alloys at room-temperature and also show good creep resistance at temperature up to 600 °C.



**Fig. 2.4 Pseudo-binary  $\beta$  isomorphous phase diagram indicating the positions of metastable and stable beta titanium alloys [31].**

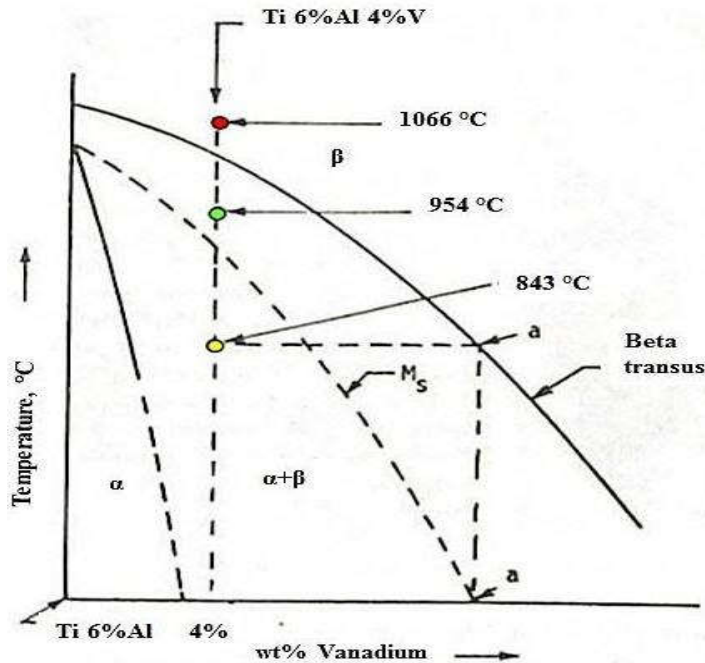
The alloys with compositions between the point of intersections of the  $M_s$  and  $\beta$  transus line ( $\beta_s$ ) at room temperature axis are commonly referred to as metastable  $\beta$  titanium alloys (Fig 2.6). More highly alloyed compositions to the right of  $\beta_s$  are considered to be stable  $\beta$  alloys. On quenching, instead of forming martensite,  $\beta$  alloys form the metastable  $\beta$  phase due to the presence of sufficient amount of beta stabilizers.

They can achieve very high strengths and are the most easily mechanically formed titanium alloys due to their BCC crystal structure. However, they have relatively high density [41].

Table 2.4 Typical applications and tensile strength of the  $\beta$  alloys [31].

S.No	Alloy	YS(MPa)	UTS (MPa)
1	Ti-11.5Mo-6Zr-4.5Sn	800-1200	900-1300
2	Ti-15V-3Cr-3Al-3Sn	800-1000	800-1100
3	Ti-3Al-8V-6Cr-4Mo-4Zr	800-1200	900-1300
4	Ti-10V-2Fe-3Al	1000-1200	1000-1400

$\alpha+\beta$  alloys contain  $\alpha$  phase stabilizing elements with 4-6% of  $\beta$  stabilizing elements and have  $\alpha+\beta$  microstructure, with primary  $\alpha$  (HCP) and retained  $\beta$  (BCC) phase. In the group of  $\alpha+\beta$  alloys, Ti-6Al-4V alloy is the most popular titanium alloy. More than 50% of all the alloys in use today are of this composition [Boyer, (1996)]. Desired microstructure and properties are obtained through annealing, quenching and tempering. Fig. 1.7 shows ternary phase diagram of Ti-6Al-V alloy. In Ti-6Al-4V, Al is  $\alpha$  phase stabilizer while V is beta stabilizer.



**Fig 2.4 phase diagram of ti al v alloy**

Among the two type of crystal structure, the alpha structure has a very low deformability on the other hand  $\beta$  phase shows good improvement in that. Due to the limited deformation capability of dense packing, the hexagonal crystal structures, is less ductile compared with body-centered cubic This is a because the hcp crystal system has 3 slip systems, while bcc crystal systems have 12 , which thereby increases the number of dislocation glide opportunities by a ratio of four. Although alpha phase has a slip plane packing density of 91 % compared to 83 % for beta phase, but the more energy is required for the activation of the slip planes as a result favorable plastic deformation in the beta phase.

Another problem with the alpha phase is that it has a hexagonal structure and only have four independent slip planes instead of five which is necessary required for homogeneous plastic deformation so making it tremendously hard to form [42].

Although, the variety of Titanium alloys may be produced by alloying different elements in titanium; however the Ti-6Al-4V alloy was the most adopted alloy from desired mechanical point of view and was mainly used in aerospace industries because of its high temperature application. Although the alloy Ti-6Al-4V was initially made for aerospace applications, but because of its high corrosion resistance and excellent biocompatibility properties it was also being used in biomedical field.

Also the mechanical strength as well as elastic stiffness of titanium alloys is very key factors for their long-term life of implants to be used as bioimplant. Simultaneously achieving the fatigue strength along with lower Young's modulus is somewhat typical due to opposite natures of properties, i.e. when the bonding force between atoms is considered [43]. A Palmquist et al. showed that Ti6Al4V with and without porous structures demonstrate excellent long term soft tissue biocompatibility and a high degree of osseointegration [44]. Corrosion resistance of Ti-6Al-4V clinically-relevant acid etched surfaces was investigated by electrochemical techniques .M. Koike et.al also assessed the biological response to several novel titanium alloys Ti-6Al-4V, Ti-13Cr-3Cu, Ti-1.5Si and Ti-1.5Si-5Cu and have been found to have low toxicity because of their corrosion resistance [45]. Y. Fan et.al investigated the role of microstructure on mechanical and fatigue properties of thin section Ti6Al4V. They found that at 1050<sup>0</sup>C water quenching transformed the equiaxed microstructure into acicular martensite microstructure. The martensitic sample exhibited the highest increases in hardness (419 HV) and 0.2% proof stress (13.8%) compared to the AR sample but at the cost of a reduction in ductility (42.7% lower elongation compared to the AR sample [46]. Tensile and bending strengths decreased with increasing annealing time, whereas the elastic modulus and bending

modulus showed no significant difference with an annealing time of up to 7.2 ks but slightly decreased at 36 ks [38]. Studies have confirmed that this alloy will undergo satisfactory osseointegration especially when treated to enhance the oxide layer on the surface [47–49].

#### **2.4 Drawbacks of widely used implants and attempt to recover.**

The alloy Ti-6Al-4V had been proven to be the best one from corrosion and mechanical point of view but still faces the drawback that all the metals do not have bio functionality. In orthopedics, bone bonding is required in the stem and acetabular cup of artificial hip joints. If the surface properties are not capable of leading to formation of a stable bonding between the surface of the implant and the surrounding tissue, this results in the formation of a fibrous layer which would undermine the load transmission between bone and implant, and would favor micro movements, eventually leading to implant failure. In the case of dentistry, hard-tissue compatibility for bone formation and bone bonding, soft-tissue compatibility for adhesion of gingival epithelium, and an antibacterial property for the inhibition of bacterial invasion are required in the implants. To promote biocompatibility and add bio function to metals, surface modification or surface treatment is necessary. For these purposes, a variety of surface treatment techniques have been investigated at the research level, and some of them have been commercialized [50]. These include hydroxyapatite, biomimetic calcium phosphate coatings; biomolecule functionalized coatings, as well as a mixture of morphological changes and coatings for a combined synergistic effect. These processes can be achieved by the number of methods such as mechanical methods, Chemical methods, Sol gel deposition, CVD, biochemical method, electrochemical method and physical methods [51]. For example, hydroxyapatite

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(HA) is considered one of the most effective bioactive materials and can be easily deposited by immersion of the implant surface in different simulated body fluids. Biochemical methods [23, 52] provide the possibility of adding and bonding specific biomolecules at the implant surface. These treatments are focused on controlling and guiding the complex sequence of biochemical phenomena that take place at the interface between an implanted device and biological tissue, such as Osseo integration. A plasma-sprayed titanium surface is thought to be suitable for bone ingrowth. The materials can endure shear forces that can break the bones. Lee et al. showed that a Nano sized porous layer of sodium titanate ( $\text{Na}_2\text{Ti}_5\text{O}_{11}$  or  $\text{Na}_2\text{Ti}_6\text{O}_{13}$ ) was formed on the surface of the plasma sprayed titanium implants after alkali and heat treatments. The average pore size on the surface of the alkali- and heat-treated implant was about 150 nm.

Hydroxyapatite may reach up to 10 mm after 2 weeks in simulated body fluid. The sol-gel process is also widely used to deposit thin (<10 mm) ceramic coatings. Compared to conventional thin film processes, it allows for better control of the chemical composition and microstructure of the coating, preparation of homogeneous films, reduction of the densification temperature, and finally simpler equipment and lower cost. Many coatings, such as titanium oxide ( $\text{TiO}_2$ ), calcium phosphate (CaP), and  $\text{TiO}_2$ -CaP composite have been prepared on titanium and its alloys for biomedical applications. Some silica-based coatings have also been produced using the sol-gel technique. Li et al. also demonstrated the precipitation of bone-like hydroxyapatite on the surface of sol-gel titania coating. The thickness of the bone-like

All these materials have an excellent capacity to bond with the living tissues. But the problems associated with the coated alloys are poor adhesiveness, non-uniform coating and the difference in the thermal coefficient of the metal substrate and coating material [55].

Although the Ti-6Al-4V alloy coated with bio coating is most suited orthopedic implant but it still suffers some drawback and biological side effects in long term clinical use. Firstly, the elastic modulus is not closely matched with the existing bones which cause the stress shielding effect and secondly negative biological impact of Aluminum and Vanadium metal ions into the body. To encounter these effects, the different composition of Ti alloys has been researched in the literature.

Ken Cho et. al have chosen Iron and Copper to replace aluminum and vanadium. They observed that Ti-Fe-Cu alloys consist of the beta Ti phase and dendritic TiFe intermetallic phase. Modulus of elasticity of the alloys increases with change in alloy composition from 110 GPa (Ti-18Fe-18Cu alloy) to 145 GPa (Ti-30Fe-2Cu alloy) with increasing atom ratio and the area fraction of the TiFe intermetallic phase. However, the decrease in Young's modulus is observed or slightly decreased with the area fraction of the TiFe intermetallic phase. The Vickers hardness of the as-cast alloys increases from 490 HV to 550 HV (Ti63.4Fe30Cu6.6 alloy). On the other hand, the Vickers hardness of the heat-treated alloys is lower than that of the as-cast alloys, despite the increase in the area fraction of the TiFe intermetallic phase after the heat-treatment [56].

V. Brailovski et.al have taken Nb and Zr in Ti alloy system and observed that Ti-Nb-Zr samples when treated at 600 °C showed the increased fatigue resistance. Tensile, compression and bending testing results indicated that Young's modulus of Ti-Nb-Zr

foams decreases when annealing temperature increases from 450 to 600 °C, Young's modulus decreases from  $10 \pm 2$  GPa to  $6 \pm 1$  GPa [57].

Abdelrahman H. Hussein et.al has demonstrated the effect of Ta and Nb systems on the young's modulus and ductility. They observed that Young's modulus decreased from 71 GPa to 60 for the most stable  $\beta$  alloy TNTFO. This reduction in Young's modulus was accompanied by an increase in the ultimate tensile strength (UTS) and hardness through the solid solution strengthening effect. The new alloys have at least 10 times lower corrosion current density ( $0.078 \mu\text{A}/\text{cm}^2$  for TNTFO) compared to Ti-6Al-4V ( $0.686 \mu\text{A}/\text{cm}^2$ ) [59].

Pedro Fernandes Santos et.al found that the tensile strength (1162–938 MPa) and hardness (308–294 HV) of the MIM fabricated alloys Ti-9Mn alloys exhibits the best balance of ultimate tensile strength (1046 MPa) and elongation (4.7%) among the tested alloys. The elongation and tensile strength of the alloys decrease with increasing Mn content. Ti-17Mn showing a compressive 0.2% proof stresses of 1034 MPa, and a compressive strain of 50%. The Young's modulus increases from Ti-8Mn to Ti-17Mn. The lowest Young's modulus corresponds to Ti-8Mn (87 GPa). However, the values for Ti-9Mn (89 GPa), Ti-12Mn (96 GPa), Ti-13Mn (99 GPa), Ti-15Mn (98 GPa) and Ti-17Mn (103 GPa) are all lower than that for annealed Ti-64 ELI (110 GPa) [60].

Josef Stráský et.al have studied the Ti-Nb-Zr-Ta based alloys and the effect of reinforcing Fe, Si and O have also been seen on said alloy system. Alloying by Fe and O significantly increased elastic modulus, a 20% increase in strength and a 20% decrease in the elastic modulus when compared to the common Ti-6Al-4V alloy was achieved in TNTZ-Fe-Si-O

alloys. The yield stress reaches 1000 MPa while the UTS reaches 1200 MPa, which significantly exceeds the tensile strength of the most used Ti-6Al-4V alloy [61].

Keiki Miura et.al have also tried new composition of ti alloy. They have studies the Ti- Nb and Sn alloy system and found that there is considerable change in the mechanical properties of alloy. The tensile strength of the Ti-Nb-Sn alloy was increased to a level greater than that of Ti-6Al-4V alloy by heat treatment after severe cold rolling with equal level [62].

To avoid the toxicity produced by vanadium ions, it is interchanged by niobium and metals, resulting in two new dual phase Ti-based alloys, i.e., Ti-6Al-7Nb and Ti-5Al-2.5Fe [63, 64]. The mechanical properties of newly developed alloys have improved little bit but the modulus of elasticity was still the problem when compared to human bones. It has been found in literature that alloy system containing alpha and dual metallurgical phases ,must be having high young's modulus while beta phase may have some low level of young's modulus as compared to alpha phase.

So low modulus  $\beta$ -type Ti-based alloys may suit the requirement of bioimplant. A lot of attempts occurs in this area [65-67] to alleviate the stress shielding effect, among which the representatives are Ti-15Mo, Ti-13Nb-13Zr, Ti-12Mo-6Zr-2Fe, Ti-35Nb-5Ta-7Zr, and Ti-29Nb-13Ta-4.6Zr [68-70].

In an attempt to find toxic free biomedical alloy, Hsueh-Chuan Hsu has also studied the Ti-Si alloy in this context. They varied the amount of silicon from 1% to 12% and have found that the bending strength of Ti-5Si was about 2.6 times that of c.p. Ti, and both Ti-10Si and Ti-12.5Si had the highest bending moduli, which were about 1.8 times higher than that of c.p. Ti. Additionally, Ti-1Si exhibited ductile properties and Ti-3Si and Ti-5Si had a

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combination of brittleness and ductility. When the Si content was 7.5 wt% or greater, the alloys showed brittle properties. Judging from the results of the mechanical properties and deformation behavior, Ti-1Si, Ti-3Si, and Ti-5Si can be considered highly feasible alloys for prosthetic dental applications [71].

Effect of Silicon and tin on the mechanical properties of Ti–Si–Sn alloys has also been studied. Alloying of 10 at. % Si has the maximum level of mechanical properties due to increasing volume fraction of the ( $\beta^*$ ) + Ti<sub>5</sub>Si<sub>3</sub> eutectic. On increasing tin content to 7–10 at. % also shows considerable effect on the properties due to the solid solution hardening mechanism. The elastic modulus and plasticity of all the alloys decrease with increasing Sn content. The elastic modulus for the alloys with 7–15 at.% Sn almost halves, decreasing to 65–60 GPa [72].

The quadric alloy system of Ti-Zr-Cr-Al has also been studied by Pan Wang group and has found that Ti-15Zr-5Cr-2Al alloy after several heat treatments shows change in their mechanical properties. They found that this alloy is having beta phase when in as cast condition and very small fraction of alpha phase which indicates the suppression of omega phase occurring due to Al addition. In as cast condition, its yield strength is found to be  $1148 \pm 36$  MPa and moderate Young's modulus of  $96 \pm 3$  GPa [73].

The addition of a small amount of ceramics particles such as TiB<sub>2</sub> and Y<sub>2</sub>O<sub>3</sub> into the titanium matrix is also expected to improve the fatigue strength of  $\alpha$ -type titanium alloys while maintaining a low Young's modulus. Figure 12 (Niinomi, 2011c) shows the Young's modulus and fatigue limit of TNTZ with TiB<sub>2</sub> or Y<sub>2</sub>O<sub>3</sub> additions, subjected to severe cold rolling; as a function of B or Y concentration along with those of TNTZ subjected to

severe cold rolling (TNTZCR) and solution treatment (TNTZST), and Ti-6Al-4V ELI (Ti64 ELI) [74].

In an attempt to moving from inertness to bioactivity, several researches are going on to impart the adequate level of bioactivity in the bio implants. The second generation bioactive materials have the ability to interact with the biological environment to enhance the biological response and the tissue/surface bonding.

The inertness of metal alloys towards human tissues after implantation become the major drawback itself in the way to be bioactive, as they lack direct chemical bonding between the material and host tissue. The efforts are being made to improve the Osseo integration and host response by altering the surface of the titanium. The metallic implants can be made bioactive by either coating of bioactive materials on the implant surface or to chemically modify the surface to increase the adhesion of biological entities [75].

Bioceramics became an accepted group of biomaterials for medical applications, mainly for implants in orthopedics, maxillofacial surgery and for dental implants because of their excellent wear rates, excellent corrosion resistance, and good biocompatibility. Bioceramics materials can have different responses to tissue in biological fluids, so they are divided in three main groups according to their interaction: bioinert high strength ceramics, bioactive ceramics which form direct chemical bonds with bone or even with soft tissue of a living organism, bioresorbable ceramics [76,77,78].

HA is type of ceramic material which is biocompatible and bioactive too and used as a coating in metal implants to enhance the bone healing and also to promote the interfacial bone-implant strength and stabilising the bone implant system. Kotian et al. analyzed the production of HA coatings on Ti and Ti-6Al-4V under different plasma atmospheres. Least

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crystallinity was observed in the case of HA coating done under argon/hydrogen followed by nitrogen/hydrogen. In the case of argon and nitrogen atmospheres, the crystallinity value was between 61% and 63%. Reaction products such as  $\text{CaTi}_3\text{O}_4$ ,  $\text{Ca}_2\text{V}_4\text{O}_9$ ,  $\text{Ca}_4\text{Ti}_3\text{O}_{14}$ , and  $\text{H}_2[\text{Ti}(\text{PO}_4)_2]$  formed support chemical bonding between HA and the metal substrate. However, the major drawback of the HAp coatings is that they cannot maintain long-term stability, and in certain situations delamination of the HAp coatings from the alloy occurs due to their poor bond strength and insufficient chemical stability.

In an attempt to find appropriate bioactivity, L.L. Hench developed the special classes of bioactive glasses, in 1970, which showed the bonding with the living tissues. Hench aimed to create a material that was biocompatible and formed a lasting bond with the host tissue when treating wounds. The original 45S5 composition consists of 45wt%  $\text{SiO}_2$ , 24.5wt%  $\text{CaO}$ , 24.5wt%  $\text{Na}_2\text{O}$ , and 6.0wt%  $\text{P}_2\text{O}_5$  and was strategically selected by Hench to facilitate bone formation while maintaining glass characteristics [79].

When these glasses were put in contact with biological fluids, a layer of hydroxyapatite (HA) analogous to the mineral phase of bones was deposited on their surface. Collagen molecules were incorporated into this layer and a biological bond could be formed [79].

With a relatively low Si content compared to more structurally sound silicate glasses, the Bioglass network degrades in aqueous solutions. The modifying elements (Na, Ca, P) are subsequently released into the surrounding physiological fluid, where the 5-stage process of the hydroxyapatite (HA) layer formation begins. Once a stable boundary of interface is established, these glasses produce the vast biological responses that may include new tissue growth, angiogenesis, and bactericidal action [80, 81]

HA formation begins when  $\text{Na}^+$  and  $\text{Ca}^{2+}$  react with  $\text{H}^+$  from the surrounding physiological fluid which raises the pH creates silanols (Si-OH) groups on the glasses surface. The rise in pH disrupts the Si network and releases silicic acid  $\text{Si}(\text{OH})_4$  which aids in silanol production. The silanols are re-polymerized to form an amorphous silica gel layer. Calcium ( $\text{Ca}^{2+}$ ) and Phosphate ( $\text{PO}_4^{3-}$ ) groups react with hydroxyl ( $\text{OH}^-$ ) and carbonates ( $\text{CO}_3^{2-}$ ) resulting in a crystalized HC layer on the glass surface [82].

The rate of bonding of bioactive glasses depends on many factors. One is the bulk composition and the most rapid rates of bonding for bioactive glasses composed of  $\text{SiO}_2$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{O}$  and  $\text{P}_2\text{O}_5$  are obtained with  $\text{SiO}_2$  contents of 45-52% by weight. In this compositional range, bonding of implant to soft and hard connective tissue occurs within 5 to 10 days [83].

Bioactive glasses or glass ceramics containing 55-60%  $\text{SiO}_2$  require a longer time to form an interfacial bond with bones and do not bond to soft tissues. Glass compositions with more than 60%  $\text{SiO}_2$  do not bond either to bone or soft tissues and they elicit formation of a non-adherent fibrous interfacial capsule.

Since then many bioactive glasses and ceramics of different composition have been produced and investigated for bioactivity and the coating purpose. Many new glass compositions have been proposed and found several biomedical applications from dental filling, drug delivery, and coating to load-bearing metal implants, to tissue engineering. But the problems associated with the coated alloys are poor adhesiveness, non-uniform coating and the difference in the thermal coefficient of the metal substrate and coating material.

So in this research work, we attempted to avoid coating also and tried to reinforce the ceramic bioactive glasses into the matrix itself rather than coating the implant surface. The idea is to use the leaching properties of glasses to cover up the implant surface with bioactive component. So two different bioactive glasses i.e borate based and silica based are used for the reinforcement in ti alloy matrix to achieve the above aim.

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