Phase transformations in titanium biomedical materials

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Abstract: *New types of materials have been developed for years, including titanium-based alloys, which have the potential for various applications. Due to the combination of their very good mechanical properties with outstanding corrosion resistance and excellent biocompatibility, titanium alloys are developing into materials that can be used in aerospace, automotive, energy systems and especially in medicine. A fundamental understanding of the phase transformations that occur at high temperatures in all these cases, especially during cooling from elevated temperatures, is necessary to achieve optimal mechanical properties of titanium alloys. It is known that the mechanical properties of titanium alloys depend on a significant extent upon the microstructure. Therefore, it is very important to understand the nature of the phase transformations that occur under different heat treatment conditions the leads to microstructure development of titanium alloys microstructure. The aim of this article is to review the current state of knowledge and previous research and to point out some of the most interesting phase transformations of titanium alloys.*

Keywords: *TITANIUM ALLOY, BIOMEDICAL MATERIALS, PHASE TRANSFORMATIONS, MICROSTRUCTURE*

1. Introduction

About 70-80% of the different types of implants are made of metallic biomaterials. Metallic biomaterials are extremely important for the reconstruction of damaged tissue, especially hard tissue, which is associated with an improvement in the patient's quality of life. Considering the fact that the world population is ageing and the elderly population is at greater risk of hard tissue failure, the demand for metallic biomaterials has been increasing rapidly for years. Research has shown that the mechanical and biological biocompatibility of metallic biomaterials needs to be greatly improved in order to reduce the number of failed operations. The biofunctionality of metallic biomaterials also needs to be improved, which is the goal of future research [1]. Depending on the specific application, biomedical materials can be used in different parts of the human body, e.g. as intravascular stents, heart valves, heart simulators and replacement implants in knees, hips, elbows, shoulders and also in dentistry. In the elderly population, implants are most commonly used for hip replacement. These diseases worsen over time and lead to a gradual deterioration of the mechanical properties of the bone due to the loss of its self-healing function and excessive loading [2].

Metals have been considered promising materials in various industries for years [3]. Today, many metals are known that are characterized by good properties and possibilities for various applications. Some of the metal studied are iron, aluminium, nickel and titanium.1 In addition to their good properties, iron alloys also have some disadvantages, such as their large mass. Steel decomposes slowly and has a higher stiffness than bone, but is highly biocompatible. The decomposition of steel occurs through the mechanism of corrosion, which occurs when a metal sample comes into contact with human body fluids through electrochemical dissolution [4,5]. The porous structure of steel is one way to improve corrosion in these alloys [6]. Another known metal is aluminium. The potential toxicity of aluminium alloys has been the subject of debate throughout history. When aluminium ions are released in significant quantities, they can have neurotoxic effects and contribute to diseases such as Alzheimer's, multiple sclerosis and dementia in Parkinson's patients [7]. Second popular metal is nickel, which is often used as alloying element for stainless steel. Today, however, nickel is considered a high-risk element due to incompatibilities. For this reason, nickel is avoided as far as possible as an additive for metallic biomaterials [1]. For these reasons, researchers are looking for other, more favorable materials to solve these problems [8]. One metal that has recently attracted the interest of more and more scientists and researchers is titanium [9].

Titanium is the fourth most abundant structural metal in the earth's crust, behind only iron, aluminium and magnesium [10]. Pure or elemental titanium has a relatively low density and a low modulus of elasticity as well as low thermal conductivity. Its properties also include high reactivity with various elements as well as good strength and good corrosion resistance. Tab. 1 shows selected properties of titanium compared to some competing metals such as iron, aluminium and nickel [9]. In order to obtain alloys that are suitable for biomedical purposes, copper is increasingly being added to titanium as an alloying element [11].

Copper is an essential trace element in the human body. It not only has strong antibacterial properties, but also offers good ductility and hardness. The addition of copper gives the alloys improved corrosion resistance, which is a significant advantage for these alloys. The antibacterial effect of Ti-Cu alloys depends largely on the copper content. Too high a copper content can cause various problems, including cytotoxicity. It can therefore be said that the copper content plays an important role in the development of new biomedical alloys [11].

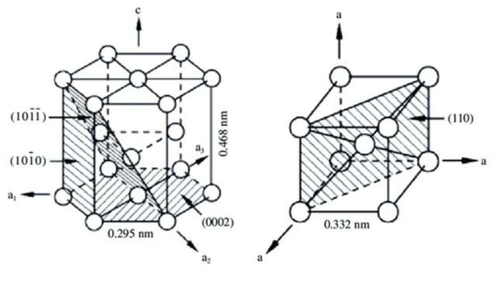
Table 1: *Physical properties of titanium compared to certain metals [9].*

Metals	Ti	Fe	Al	Ni
Density (g/cm^3)	4.5	7.9	2.7	8.9
Elastic modulus (GPa)	115	215	72	200
Melting point (°C)	1670	1538	660	1455
Thermal conductivity (W/mK)	15-22	68-80	221-247	72-92
Corosion resisatnce	high+	low	high	medium
Reactivity with oxygen	high+	low	high	low

2. Crystal structures of titanium

Pure titanium can crystallize in different crystal structures in a wide temperature range. A complete transformation from one crystal structure to another, where the "transition temperature" is the corresponding transformation temperature, is called an allotropic transformation [12]. Titanium can occur in the form of two crystallographic structures (Fig. 1), namely: α-phase, which has a hexagonal close-packed (hcp) crystal structure, and β-phase, which has a cubic volume-centered (bcc) crystal structure.

At 883 °C, titanium undergoes a temperature transformation from a hexagonal close-packed to a cubic volume-centered structure, which remains stable up to the melting point, i.e. a temperature transformation from the α to the β phase takes place [13,14].



a) b)

Fig. 1 Crystal structures of a) α (hcp) and b) β (bcc) titanium[15].

Fig. 1 a shows the hexagonal close-packed crystal structure at low temperatures together with the three most densely packed lattice planes and the lattice parameters shown at room temperature. The resulting ratio c/a = 1.587 for pure α-Ti is less than the ideal ratio for the hcp structure with c/a = 1.633. Fig. 1 b shows the unit cell of the bcc β phase. The figure shows one variant of the most densely packed {110} lattice planes as well as the lattice parameter of pure β-Ti at a temperature of 900 °C [16]. When alloying elements are added to titanium that increase the stability of the α phase at higher temperatures, they are called α stabilizers, while on the other hand, β stabilizers can be added that increase the stability of the β phase at lower temperatures. Neutral elements, on the other hand, have no influence on the transformation temperature [17]. Fig. 2 shows different categories of titanium phase diagrams formed with different elements. Ultimately, each element added to pure titanium will determine the mechanical properties by affecting the stability of the α and β phases [18].

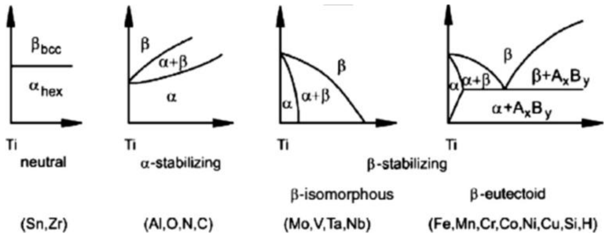


Fig. 2 Different phase diagrams formed with different elements [18].

α –stabilizers

α–stabilizers are both substitutional and interstitial alloying elements. Substitutional α stabilizers are elements such as germanium, aluminum and gallium while interstitial α stabilizers are nitrogen, oxygen and carbon. Of the above substitutional alloying elements, aluminum is the most widely used, since it has a high solubility in the α and β phases. Aluminum also reduces the density of the alloy. The addition of aluminum in titanium alloys is limited to 5-6 wt. % since with increasing aluminum content, the Ti-3Al (α2) phase will form, while at about 5 wt. % aluminum, a two-phase region α + Ti-3Al is formed. The formation of the Ti-3Al (α2) phase makes titanium alloys brittle. Although their solubility is much lower than aluminum and oxygen, other substitutional alloying elements are rare earth elements such as scandium, yttrium and lanthanum. On the other hand, oxygen, carbon and nitrogen are considered extremely strong α-stabilizers. Carbon has a much lower solubility in the α phase than oxygen or nitrogen. These alloying elements tend to harden the alloy, but also reduce the ductility of titanium alloys. Commercially pure titanium at room temperature consists primarily of the α-phase. As alloying elements are added to titanium, they change the amount of each phase present and the temperature of the β transition [19].

β-stabilizers

Since during heating at a temperature of about 883 °C α transforms into a β structure, this transformation temperature can be raised or lowered depending on the type and amount of impurities or additions of different alloys. β-stabilizers are transition (Fig. 2) metals and are divided into two categories: β-isomorphous and β-eutectoid. β-isomorphic stabilizers have complete solid solubility with β Ti and some of them are vanadium, niobium and molybdenum. Elements such as tantalum and tungsten are rarely used due to their density. Among the β-eutectoid stabilizers commonly used for alloying with titanium are silicon, iron, chromium, while nickel and manganese have very limited use. Hydrogen is an element that has a low eutectoid temperature of 300°C and forms a β eutectoid, i.e. it stabilizes the β phase. Chromium is limited to 5 wt. % because otherwise an undesirable $TiCr_2$ intermetallic compound will form. Similar to chromium, the amount of iron is also limited to 5.5 % by weight. On the other hand, silicon is a common alloying element for titanium alloys at high temperatures [12]. Elements such as silicon and iron increase the strength and reduce the ductility of titanium products. A well-known and useful parameter for a given titanium alloy composition, which characterizes the stability of the β phase, is the molybdenum equivalent ([Mo]eq). It is a quantitative measure of the combined effects of β phase stabilizing elements, α phase stabilizing elements, and neutral elements contained in titanium alloys on β phase stability [18]. In addition to the mentioned α and β stabilizers, there are also some neutral elements such as, for example, tin, zirconium, silicon used for some purpose other than the enhancement of α and β phases such as strengthening or processing [20,21]. The mentioned elements are added to metastable alloys of the β Ti phase because they are considered to change the kinetics of the hexagonal isothermal formation of the ω-phase during aging, which in turn stabilizes the bcc β-phase. Some studies have shown that the addition of zirconium or tin to binary Ti-V alloys reduces the volume fraction of the isothermal ω-phase and suppresses its nucleation in sufficiently high concentrations. Similar results were observed in the same study only for the addition of zirconium in binary Ti-Mo alloys [22].

3. Classification of titanium alloys

Ti alloys are categorised into three basic types depending on their phase composition, namely:

- α-Ti alloys,
- α+β Ti alloys,
- β-Ti alloys.

There are two main groups of α-Ti alloys, namely super-α and near-α-Ti alloys. Super-α alloys contain a large amount of α-stabilising alloying elements, more than 5 wt. %. These alloys consist entirely of α-Ti grains. Another type of these alloys, the near-α alloys, contain a large amount of α-stabilisers with a lower amount of β-stabilising elements of less than 2 wt. %. The microstructure of these alloys consists of a small volume fraction of β-Ti grains distributed between a much larger volume fraction of α-Ti grains. They are characterized by better hardness properties compared to super α-Ti alloys [23]. Nearly α-Ti titanium alloys are highly valued for their low density, exceptional strength and corrosion resistance. They are suitable for applications in the aerospace, automotive and medical technology industries. They also have good resistance to high temperatures and are therefore suitable for use in extreme temperature conditions. Alloys close to α-Ti offer an excellent weight-to-strength ratio, enabling the production of lightweight components while maintaining structural integrity. This is one of the key benefits in aerospace applications for improved fuel efficiency and performance even at temperatures up to 540 °C [24]. When using these alloys at elevated temperatures from 300 °C to 650 °C, interactions between α-Ti alloys and salts present in the atmosphere above the ocean can lead to limitations in application and a reduction in service life. An adjustment of the types and contents of certain alloying elements is necessary to improve the corrosion and mechanical properties of α-Ti alloys. Alloying elements such as molybdenum and copper have been added to develop high-temperature titanium with high heat resistance and good oxidation behavior up to 600 °C [25]. hey are generally used in non-structural applications where good corrosion resistance and low strength are required [22] The main hardening mechanism of α-Ti alloys is the formation of solid solutions, texture hardening and precipitation hardening through the formation of the α2 phase [20]. he modulus of elasticity and yield strength of α-Ti alloys are between 102 and 104 GPa and 170 and 485 MPa respectively. The maximum tensile strength is in the range of 240 to 550 MPa. α-type Ti alloys are not used as implants due to their low mechanical strength at room temperature. Nevertheless, commercially pure titanium belongs to the first generation of biomedical materials that were used as biomaterials for dental and other medical applications [26].

Ti α+β alloys contain between 4 and 16 % β stabilisers [27]. These are two-phase alloys that contain a mixture of both phases. They are most commonly used for applications that require good toughness, higher strength and excellent corrosion resistance [22]. At room temperature, α+β alloys usually contain 10-20 % β phase [28]. Nearly β-alloys, also known as metastable β-alloys, contain a small amount of α-stabilisers and 10 to 15 % of β-stabilisers. β - stabilisers promote the retention of the β-phase in a metastable state at room temperature. The alloys can be heat treated by ageing, resulting in the deposition of a very fine α-phase dispersed in the β-matrix [27]. In addition to all the properties mentioned above, these alloys with α+β also exhibit the ability for rapid osseointegration in the body [29]. The combination of higher strength and density of 4.5 g/cm^3 and phase stability results in excellent specific properties that extend up to high temperatures of around 600 °C [30] The best-known alloy is the biomedical Ti-6Al-4V, which accounts for 50 % of titanium production. In the Ti-6Al-4V alloy, vanadium is a stabiliser of the β-phase. The alloy had good mechanical properties, but it was later discovered that aluminium and vanadium are not biocompatible and cause irritation and various diseases [14]. The first generations of alloys without harmful effects on the human body were alloys containing non-toxic components such as molybdenum, niobium and iron [20,26].

β-Ti alloys are one of the most versatile groups of materials in terms of their microstructure, mechanical properties and processing. These alloys include stable β-, metastable β- and β-rich α/β-alloys. They offer an alternative to α/β alloys due to the better heat treatment options. They have a wide range of strength-to-weight ratios as well as some other good properties such as a low modulus of elasticity, reasonable biocompatibility and high corrosion and wear resistance. Compared to α/β alloys, β-Ti alloys have better fatigue resistance [31,32].

Compared to α+β alloys, these alloys contain larger amounts of β stabilisers such as zirconium and tantalum, molybdenum and smaller amounts of α stabilisers without the formation of intermetallic phases [20]. To improve their strength, they can be heat-treated at temperatures between 450 and 650 °C due to the partial transformation of the β-phase into the α-phase. Increasing the β-phase content in β-type Ti alloys can improve some properties such as plasticity, toughness and heat treatability and, on the other hand, reduce the modulus of elasticity. Compared to α+β-type Ti alloys, these alloys have better biocompatibility and are considered to be more corrosion resistant in the human body [26]. Most β-type Ti alloys have a higher density than other types of Ti alloys due to the higher content of alloying elements such as niobium, molybdenum, tantalum and zirconium [33] These elements are quite rare, which leads to higher raw material costs for alloy production. Some of the β-Ti alloys used are Ti-15V-3Cr-3Al-3Sn, Ti-15Mo-2.7Nb-3Al-0.2Si, Ti-3Al-8V-6Cr-4Mo-4Zr and Ti-10V-2Fe-3Al alloys [34]. Due to certain difficulties in the production of β-Ti alloys, researchers have focused on the development of new, cheaper alloys consisting of alloying elements such as manganese, chromium, iron and tin, which are cheaper but also have good mechanical properties for biomedical applications [35]An important prerequisite for the use of these alloys in biomedicine is their non-toxicity. β-Ti alloys can be used as viable alternatives in the manufacture of dental implants. Due to their high strength and low density, these alloys are excellent structural materials for use in airplanes. The choice of alloy constituents and the desired properties of titanium alloys are controlled by application-specific design criteria [32]. These alloys can be used in the construction of power plants, but also in the automotive industry and in the manufacture of sports equipment [36].

4. Phase transformations of Ti-Cu alloys

Cast Ti-Cu alloys have been studied for many years [37]. To date, many studies have been carried out on the binary Ti-Cu phase diagram and on the possibilities of different titanium and copper contents in the alloys. The Ti-Cu binary phase diagram shown in Fig. 3 shows the possibility of obtaining multiple intermetallic phases, while Tab. 2 contains the crystal structure data of the Ti-Cu alloy, which is discussed below [37,38,39].

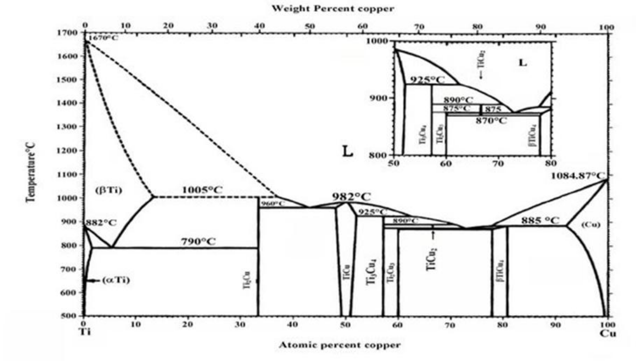


Fig 3: *Ti-Cu binary phase diagram [37,38].*

Table 2: *Data on the crystal structure of Cu-Ti alloy[39].*

Phase	Composition, wt% Cu	Pearson symbol	Space group
(α Ti)	0 to 2.1	hp2	P63/mmc
(β Ti)	0 to 17.2	cl2	Im3m
Ti2Cu	39.9	tl6	l4/mmm
TiCu	55 to 59	tP4	P4/nmm
Ti3Cu4	63.9	tl14	l4/mmm
Ti2Cu3	67	tp10	P4/nmm
TiCu2	72.7	oC12	Amm2
TiCu4	83 to 84.9	oP20	Pnma
αTiCu4	-83 to 84.9	tl10	l4/m
(Cu)	94 to 100	cF4	Fm3m
Metastable phases			
TiCu3		oP8	Pmnm
B“		tP2	P4/mmm

The most interesting point of the Ti-Cu diagram is that in previous studies, two different versions were published about the stability of different intermetallic compounds on both the Cu-rich side and the Ti-rich side. Some researchers spoke of the existence of Ti_3Cu and others of the existence of Ti_2Cu as a stable equilibrium phase.

In 1912, the first study on the Ti-Cu binary alloy system was conducted, and the results showed large impurities in the alloy, so the results were inconclusive. In addition, in 1939, Laves and Wallbaum first identified the intermetallic compounds Ti_2Cu and $TiCu_3$ in the binary phase diagram of Ti-Cu, and over the years of research, four new intermetallic compounds Ti_2Cu, TiCu, Ti_2Cu_3 and TiCu were identified through various heat treatments [40].

Canale et al [40] proved the existence of the Ti_3Cu phase as a stable phase together with six previously identified stable intermetallic compounds when investigating Ti-Cu alloys with a Ti content of more than 75 at [40].

Qin et al [41] demonstrated in their studies that the Ti_2Cu phase forms in Ti-5Cu, which contains a small amount of the α’ phase at the melting boundaries, resulting in lower corrosion resistance. The heat treatment process used in this study eliminates the detrimental effect of the α' phase, and the Ti_2Cu phase is refined at different cooling rates, which improves the corrosion resistance. Heat-treated Ti-5Cu samples were found to have similar corrosion properties to pure CP-Ti. The slow cooling rate resulted in a larger gap between the Ti_2Cu phases in the microstructure. This ultimately leads to a higher corrosion resistance [41].

Zhu et al [42] proved that α-Cu_4Ti, Cu_3Ti, Cu_3Ti_2 and Cu_4Ti_3 are metastable phases, while β-Cu_4Ti, CuTi and $CuTi_2$ are stable phases at 0 K by calculating the enthalpy of formation of Ti-Cu alloys. They also found that the CuTi phase has the highest hardness, stability and brittleness among all Cu–Ti intermetallics [42].

In their investigations, Zhang et al [43] demonstrated that the Ti_2Cu phase forms in the Ti-Cu alloys investigated, which plays a key role in the antibacterial mechanism. The antibacterial effect of the Ti-Cu alloy was strongly proportional to the Cu content and Ti_2Cu phase on the surface, and high Cu and Ti_2Cu content contributed to higher strength and strong antibacterial effect [43].

Kikuchi at al [44] demonstrated that three structures are present in Ti-Cu alloys with up to 10 % Cu: α-Ti+Ti_2Cu, hypoeutectoid and hypereutectoid structure. An Ti_2Cu interface was found to form a eutectoid structure with α-Ti. No β-Ti primary phase was found. The eutectoid reaction of this alloy is relatively fast. The microstructures of Ti-Cu alloys with 1, 2 and 5 % Cu were similar to those of α-Ti. The solubility of Cu in the α-Ti phase decreases with decreasing eutectoid temperature, while the tensile strength increases with increasing copper concentration in the alloy [44].

Liu at al [45] proved in their investigations that the binary Ti-Cu alloy has a eutectoid structure at 7.0 %. A Ti_2Cu interface was found in the titanium-rich region. Alloys with a near-eutectoid structure should have lower ductility and higher strength than cp-Ti. The same study also found that Ti–Cu alloys with up to 10.0 % Cu have better tensile strength but lower ductility, while Ti–5Cu alloys have up to 2 times higher strength than cp-Ti. Studies have shown that Ti alloys with 5 and 10 % Cu have significantly higher corrosion resistance than cp-Ti [45,46].

Hayama et al [47] in their study of the Ti-Cu alloy, concluded that the β-phase cannot be stabilised after rapid cooling at low temperatures and that higher cooling rates are required for its stabilisation. The investigated Ti-5Cu alloy exhibited a martensitic microstructure. They also found that a higher copper content in the alloy increased the proportion of the intermetallic Ti_2Cu phase [47].

The results of previous studies suggest that the Ti_3Cu phase does not form during the equilibrium process and therefore does not exist as an equilibrium compound in the equilibrium phase diagram of Ti-Cu alloys.

5. Conclusion

Driven by developments and major discoveries in biomedicine in recent years, the demand for titanium and its alloys is increasing rapidly. Thanks to favourable properties such as biocompatibility, Ti-Cu alloys have become increasingly popular as biomedical materials. This article provides an overview of phase transformations in biomedical titanium materials, with a focus on Ti-Cu alloys.

5. References

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