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MICROSTRUCTURE DEVELOPMENT IN TITANIUM AND ITS ALLOYS USED FOR MEDICAL APPLICATIONS

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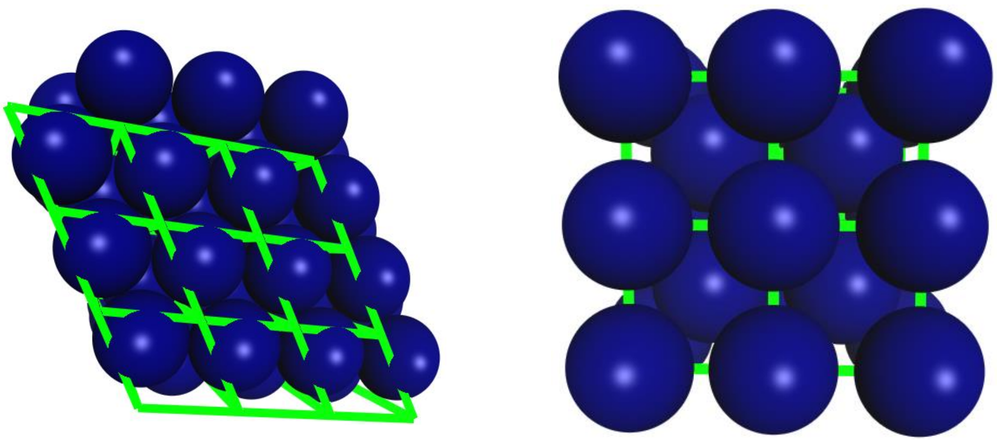
The main objective of this research is to analyze the alloying elements influence on the microstructure of titanium alloys used in orthopedic surgery using optical microscopy. Also, descriptions of the technological routes factors that influence microstructure appearance are discussed.

In our study we concluded that, given the complex geometry of the implants and various processing technologies different types of microstructures can occur, an aspect that strongly influence further specific properties.

Keywords: titanium alloys, microstructure, metallography, orthopedic implants.

1. Introduction

Titanium is an allotropic element with hexagonal closed-packed (hcp) crystal structure at room temperature and a body-centered cubic (bcc) crystal at temperature above 883°C. The hcp structure, shown in Fig. 1.a, is referred as alpha (α) phase while the bcc structure, shown in Fig. 1.b, is named beta (β) phase.



a. b.

Fig. 1 The crystal structure of a. α and b. β Titanium constructed using Accelrys Materials Studio using lattice parameters published by [1]

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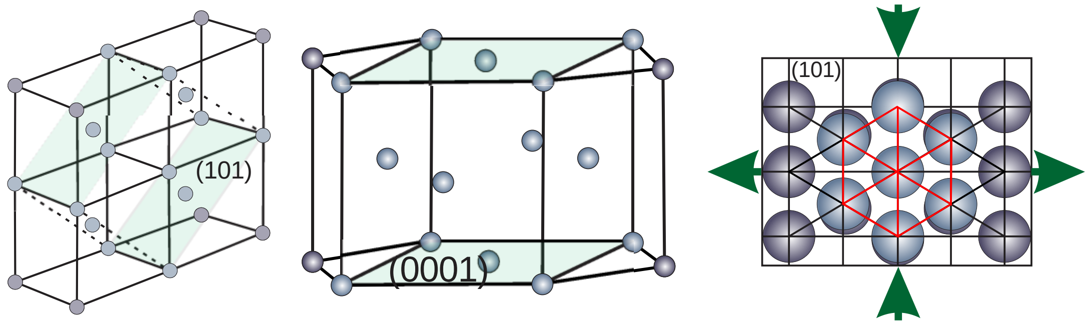
When cooled from β phase the {110} densely packed planes of the bcc structure transform to {0001} basal planes of the hcp structure [2], a schematic is shown in Fig. 2 a. and b.



a. b. c.

Fig. 2 Schematics showing β to α transformation (a. and b.) and the atomic distortion (c.)

The bcc crystal has 12 hcp variants to transform to, orientation dependant. In α phase the distance between basal planes is larger than in β and slight atomic distortion occurs, as presented in Fig. 2.c. The contraction on the c axis reduces the c/a ratio at 1.578, below 1.633, the ideal ratio for ideally hexagonal closed packed structures [2]. A macroscopic volume increase can be observed during the transformation.

Cooling rates dictate microstructure appearance. Upon cooling α nucleates on β grain boundary (Fig. 3.a) because of phase incoherency. Slow cooling rates can cause α plate nucleation either on β grain boundary (Fig. 3.b) or at β-α interface (Fig. 3.c), the resulting microstructure being described as lamellar.

a. b. c.

Fig. 3 Lamellar structure formation – schematic view

On higher cooling rates α plates nucleated on β grain boundary cannot expand throughout the whole grain (Fig. 4.a) and new plates begin to nucleate on the boundaries of other α colonies (Fig. 4.b). The resulting microstructure has a woven appearance (Fig. 4.c) and it is called “basket weave” or Widmanstätten. The thickness of α plate is reduced when cooling rates are high.

a. b. c.

Fig. 4 Widmanstätten structure formation – schematics view

In titanium and its alloys, a martensitic transformation occurs. The name is taken from steel terminology given their common features: it is time independent, proceeds without diffusion and depends solely on the cooling rate.

The martensitic transformation occurs by a cooperative shearing movement of atoms along [111]β (112)β and [111]β ($\bar{1}$01)β [3]. Similar to steel martensite, the transformed volume appears plate shaped, but frequently the collocation “disk shaped” is used. Two martensite morphologies can be observed, called alpha prime (α') and alpha double prime (α").

The α' has an hexagonal structure and in pure and low alloyed titanium appears as irregular large regions without internal features observable by light microscopy. In high alloyed titanium alloys α' has an “acicular” or “needle like” appearance and appears as individual plates.

Usually the α" appears in highly alloyed titanium alloys (at least 3 element additions). The alloying elements distort the lattice from hexagonal to an orthorhombic one.

In titanium metallurgy the alloy classification is made according to the crystal structure and also to the microstructure. Thus three main titanium alloys types can be described: α, α+β and β [2]. Some authors expand this classification into 5 alloy types: α, near α, α+β, near β and β according to the microstructure that results from processing [4-7].

The chemical composition, processing and thermal history generate a variety of microstructures that can appear in titanium alloys since multiple phase transformations are possible: some related to β-α allotropic transformations and precipitation reactions implying metastable phases.

The most common phases present in titanium and its alloys are briefly described in table 1.

Table 1

Common phases in titanium alloys

Phase/symbol	Short description	Space group
Alpha (α)	Allotropic form of titanium at low temperature with hcp structure	$P6_3/mmc$
Beta (β)	Allotropic form of titanium at high temperature, either metastable or stable in high alloyed titanium with bcc structure	$Im\bar{3}m$
Alpha$_2$(α_2)	A compound, Ti_3Al, which appears in a wide range of Al content	$P6_3/mmc$
Beta$_2$ (β_2)	Ti_2AlNb bcc phase at high temperatures with CsCl structure	$Im\bar{3}m$
Gamma (γ)	TiAl extending on a wide range of Al content and CuAu structure	P4/mmm
Alpha prime (α')	Hcp structure, a non-equilibrium phase in martensitic transformations	$P6_3/mmc$
Alpha double prime (α'')	Orthorhombic martensite	Cmcm
Precipitates	Intermetallic precipitates $(TiZr)_5Si_3$ and Ti_2Cu are most frequent	-
Beta prime (β')	Resultant of phase separation in β alloys. It is β phase with different composition than the matrix.	$Im\bar{3}m$

In Commercially Pure Titanium and α alloys the α phase is predominant with small fractions of retained β in the later. Near alpha alloys contain 1-2%β stabilizers (Mo, Ta, Nb, V) for strength improvement.

Upon cooling from β phase the transformation can occur via nucleation and growth generating the Widmanstätten structure or by martensitic transformation when the acicular α’ appears [8,9].

Alpha alloys cannot be heat treated but have excellent weldability [9]. The solid solution can be strengthened by α stabilizer (Al, O, Ga, Ge or C) or neutral alloying elements (Sn, Zr) addition. Thermo-mechanical processing is used to control grain size and texture.

The α+β alloys have a chemical composition rich in β stabilizing elements (usually 4-6%) and respond to heat treatment, thus a variety of microstructures develops [10], three main types are described in literature: fully lamellar, bi-modal and fully equiaxed [11].

A fully lamellar microstructure is obtained when a recrystallization annealing is performed at the end of the processing route. Cooling rate controls lamellae width and colony size [12].

Bi-modal structures appear post thermo-mechanical processing below β-transus temperature. Hot working is performed in the α+β phase field and α lamellae deform plastically and annealing temperature determines the volume fraction of recrystallized α. Cooling rate from annealing temperature controls the width of the lamellae [13].

A fully equiaxed microstructure is obtained when cooling from recrystallization annealing temperature is sufficiently slow to allow α grain formation. No lamellae will form within β grains [14].

The β alloys chemical composition comprises large amounts of β stabilizers, approximately 30%, making the β phase stable at room temperature if the alloying element has a bcc structure (V, Nb, Ta, Mo). Metastable β alloys contain 10-15% β stabilizing elements (Mo, V, Nb, Cr, Fe) and β to α transformation proceeds at very low rates. Aging these alloys generates a Widmanstätten microstructure of α in β. No martensitic transformation occurs in β alloys when quenched. The α phase precipitates as fine plate like particles termed platelets. This microstructure is specific to alloys with superior mechanical characteristics.

Another microstructure described in literature is the β annealed microstructure. Such microstructure is obtained post recrystallization annealing in β field followed by aging in the α+β phase field, when α nucleates on grain boundary and appears as a continuous layer [15].

Given its outstanding characteristics (lightweight, high specific strength and high corrosion resistance) titanium and its alloys are used since 1950 in the aerospace industry. Medical applications date back to 1930 for similar reasons, plus its excellent biocompatibility and low Young's modulus which makes it ideal for applications in orthopedics since less stress shielding appears on the bone.

Although various titanium alloys exist commercially, few found their use in medicine. Pure titanium and α+β alloys (most used Ti-6Al-4V) are of wide spread use as structural and functional biomaterials mainly in orthopedics [16, 17] and dentistry [18, 19], but also in cardiovascular surgery [20, 21] and neurosurgery [22, 23]. Relevant types of orthopedic implants are shown in fig. 5.

Fig. 5 Titanium and titanium alloys used in orthopedics as implants (hip implant stems, acetabular cups, nail, bone plate and screws)

Debates regarding the toxicity of some alloying elements, led to development of new alloys specific for medical use like Ti-6Al-7Nb, Ti-5Al-2.5Fe, Ti-15Mo, Ti-13Nb-13Zr, Ti-12Mo-6Zr-2Fe, and Ti-29Nb-13Ta-4.6Zr [24, 25].

The excellent compatibility of titanium and its alloys with surrounding tissue can be attributed to the stable oxide layer. The implant surface is of utmost importance for interface phenomena with human tissue. Improvements and specific surface processing for specific medical applications are performed using various coating materials and techniques in order to obtain better biocompatibility, osseointegration and bacterial control [26-31].

Each new alloy comes with its own advantages and disadvantages, but in practice for medical applications of wide use remain Commercially Pure Titanium and Ti-6Al-4V alloy type.

The samples used for metallographic characterization were obtained from various orthopedic implants, manufactured by different companies.

2. Materials and methods

Sample preparation

Titanium has a low thermal conductivity when compared to other metals and alloys, water cooling and feed rate reduction are mandatory. Cutting is usually performed using SiC disks, but diamond ones work fine as well. For the current study for sample cutting a SiC disk was used on a *Buehler Delta Abrasimet* with cutting speed of 4400rpm under intense water cooling.

The samples were then mounted using an automated mounting press *Buehler Simplimet 1000* at 290bar and 150°C with 4min heating and 5min cooling time. The samples were mounted in phenol resin.

Mechanical polishing is widely used and in following paragraphs the laboratory procedure applied when titanium or titanium alloys samples is prepared. The procedure applies to a semiautomatic method and was found to give good results.

Grinding and polishing were performed on a *Buehler Phoenix alpha with vector head* with steps specific parameters.

First step implies water cooled grinding on SiC or diamond paper up to 1200grit with platen speeds lower than 150rpm with a 40-70N force applied on the mount.

First polish can be performed on synthetic cloth with 6 or 9µm diamond suspension in an alcohol based lubricant using a 120-150rpm speed and 40-90N force applied on the specimen. Final polish can be performed on 0.04µm SiO_2 or 0.05µm Al_2O_3 suspensions at 120-150rpm and a maximum 15N force on the specimen.

The sample preparation route is given in table 2 for Commercially Pure Titanium and in table 3 for titanium alloys.

Table 2

Sample preparation parameters for Commercially Pure Titanium

Parameters	Grinding [plane/fine]	Polishing [I/II]
Abrasive and size	SiC P400, P600, P1000/Diamond, 9µm	Colloidal silica, 0.04µm
Lubricant/suspension	Water/Alcohol based	Alcohol based
Speed [rpm]	300/150	150/130
Force[N]	15/20	20/10
Time[min]	Until plane/~5min	~10/10

Table 3

Sample preparation parameters for titanium alloys

Parameters	Grinding [plane/fine]	Polishing [I/II]
Abrasive and size	SiC P400, P600, P1000/Diamond, 9µm	Colloidal silica, 0.04µm
Lubricant/suspension	Water/Alcohol based	Alcohol based
Speed [rpm]	300/150	150/130
Force[N]	40/30	30/15
Time[min]	Until plane/~5min	~5/5

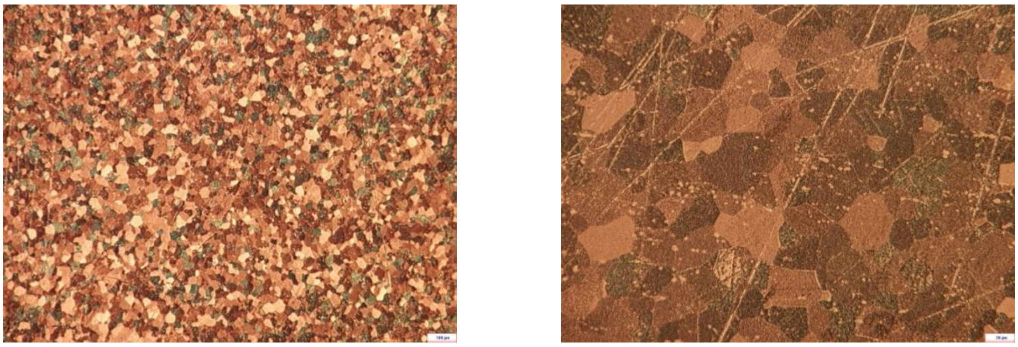
As etchant a 3ml HF (50%) + 5ml HNO_3 (65%) + 100ml H_2O solution is prepared, known as Kroll's reagent. Small amounts of hydrogen peroxide are sometimes added. Etching occurs in matter of seconds (15-25s swabbing) and, if the results are not satisfactory, final polishing and etching are repeated until all unwanted artifacts are removed.

The light microscopes used for metallographic characterization were *Reichert UnivaR* and *Olympus BX51*.

3. Results and discussion

Titanium and titanium alloy implants can be obtained by casting, by powder metallurgy and by forging, the most used processing route. Forging and specific heat treatments allow microstructure control and reproducible properties.

For Commercially Pure Titanium and α alloys a generic processing route would comprise of homogenization, deformation and recrystallization annealing. Homogenization and plastic deformation are both performed in the α phase domain since the alloying elements quantity is very low. Sometimes the homogenization step is omitted.



a. b.

Fig. 6 Uniform size α grains resulted post low temperature recrystallization annealing in Commercially Pure Titanium, a. uniform sized α grains and b. detail at higher magnification

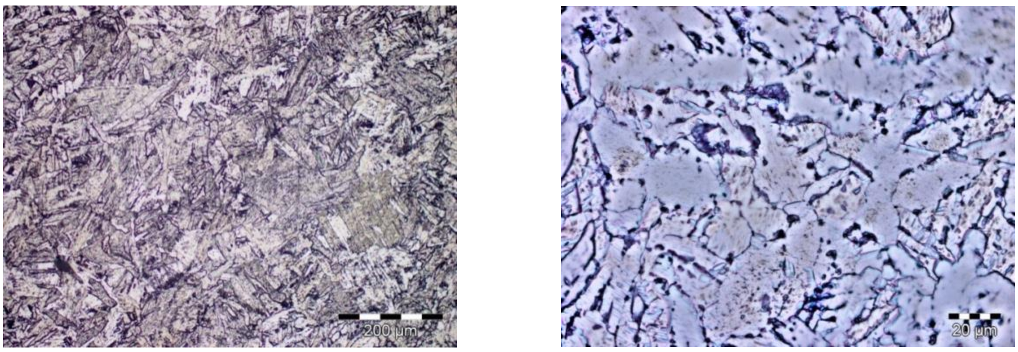
Plastic deformation of titanium and α alloys is easily performed since they are ductile and slow work hardening. Mechanical characteristics do not improve considerable by cold working and a recrystallization annealing is almost always performed.

The resulting microstructure, shown at various magnifications in Fig. 6 a. and b., consists of recrystallized α grains, obtained only by annealing of materials deformed in α phase field. In near α alloys a dispersion of β is present.

Fig. 7 Commercially Pure Titanium acetabular cup

Significant impact on resulting microstructure can be attributed to deformation degree which controls texture and grain size as well as to annealing temperature which controls the recrystallized α grain size.

Studies performed on metallographic specimens obtained from a Titanium acetabular cup (Fig. 7) revealed equiaxed α grains with a slight altered morphology, as shown in Fig. 8.a.



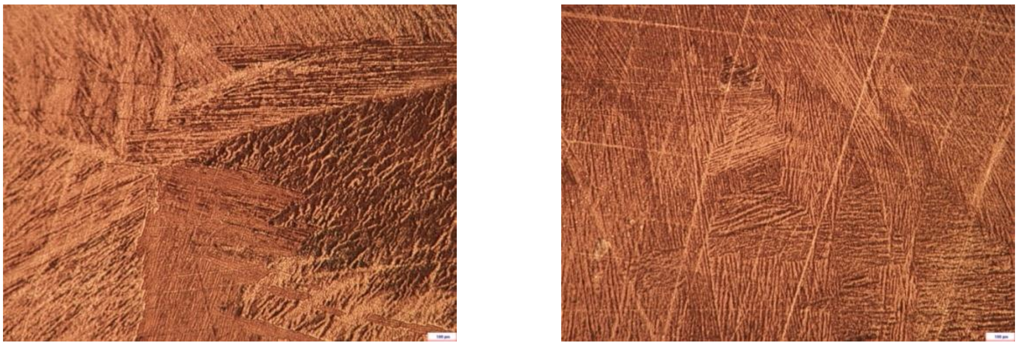
a. b.

Fig. 8 Metallographic specimen obtained from an acetabular cup showing a. uniform size α grains in Commercially Pure Titanium class 2, and b. higher magnification showing jagged edges

The α grains observed at higher magnifications (Fig. 8.b.) appear with jagged edges. The lack of deformation twins and the equiaxed morphology of the grains suggest a high temperature recrystallization annealing followed by water quenching.

When high contents O and N are dissolved in lattice interstices, as in low classes of Commercially Pure Titanium, the Widmanstätten structure becomes more obvious than higher purity classes.

Recrystallization annealing is performed usually above β transus temperature and cooling rate dictates the resulting microstructure. Slow cooling rates favors the Widmanstätten structure formation, via nucleation and growth, while fast cooling rates the β to α transformation occurs martensitically and the resulting microstructure appears plate like.



a. b.

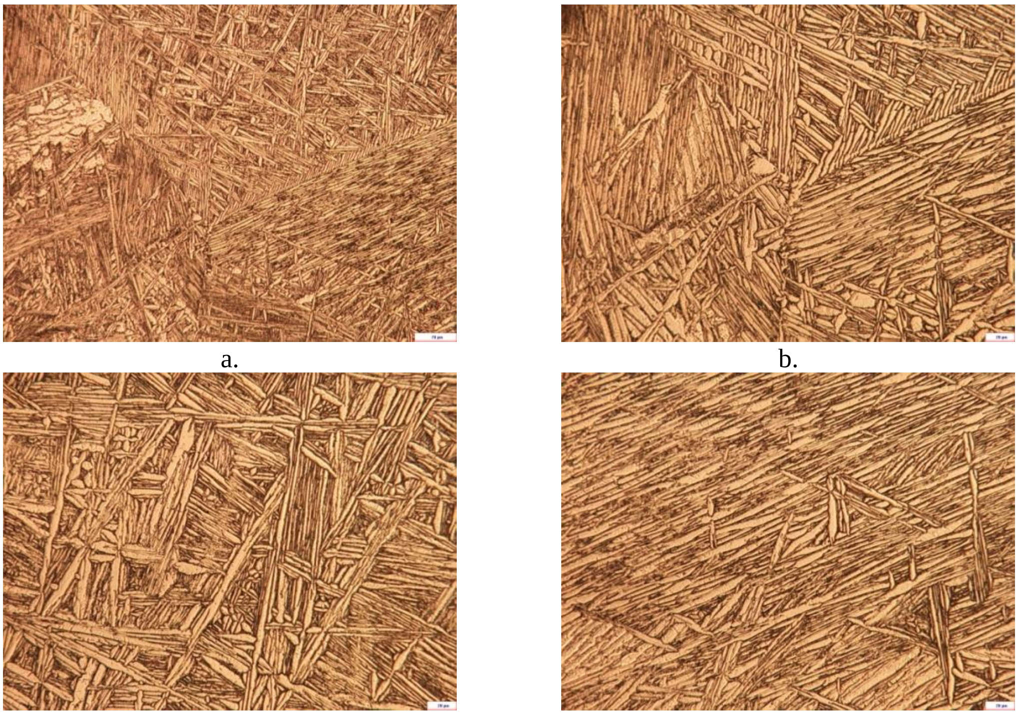
Fig. 9 Fully lamellar microstructures resulting when cooling rates are intermediate (air cooled) in an experimental titanium alloy, a. at grain boundary and b. inside the grain

Martensitic and Widmanstätten α are usually grouped together and referred as acicular α.

a. b.

Fig. 10 Fully lamellar microstructures resulting when cooling rates are high (water cooled) in an experimental titanium alloy, a. and b. different aspects at boundary triple point

Thus, in α and near α alloys the microstructure consists of α in three morphologies: equiaxed, Widmanstätten and martensitic, their occurrence depending on processing parameters: deformation and annealing temperature as well as cooling rates, as shown in Fig. 9 a. and b. for intermediate cooling rate (air) and Fig. 10 a. and b. for high cooling rate (water).



a. b.

c. d.

Fig. 11 Fully lamellar microstructure developed in an experimental titanium alloy, a. general view of the microstructure, b. lamellae forming on the grain boundary, c. lamellae weaving inside the grain and d. boundary parallel orientation of lamellae inside a grain

The microstructure of α+β titanium alloys was classified as fully lamellar, fully equiaxed and bi-modal or duplex with α equiaxed grain in the lamellar α+β matrix. These structures depend upon processing routes and parameters used.

Fully lamellar microstructures (an example shown in Fig. 11.a.) are expected when following steps are implemented: homogenization at temperatures above beta transus, plastic deformation in α+β or β phase field, followed by recrystallization and eventual aging.

On higher cooling rates α plates nucleated on β grain boundary cannot expand throughout the whole grain (Fig. 11.b and d.) and new plates begin to nucleate on the boundaries of other α colonies (Fig. 11.c).

Influence factors for microstructural features (lamellae thickness, colony size and grain boundaries) are the cooling rates when annealed. The thickness of α lamellae decreases with increasing cooling rates, similar observations apply for α colony size in a diminished manner. Prior β grain boundaries remain observable with α layers adjacent, layer thickness increasing as cooling rate decreases.

The specimen studied to exemplify microstructure type in α+β titanium alloys for medical applications stems from an acetabular cup made of Ti-6Al-4V (Fig. 12) conforming to ASTM F1108 chemical composition specifications. A porous surface is present for better osseointegration.

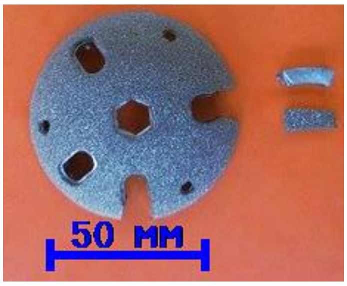
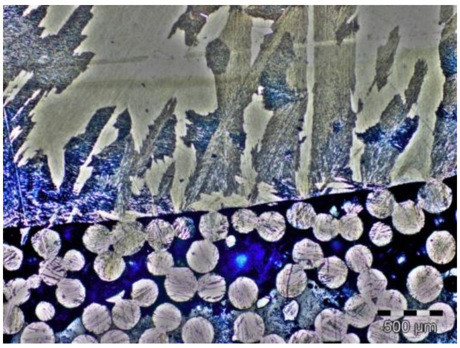


Fig. 12 Porous Ti-6Al-4V acetabular cup

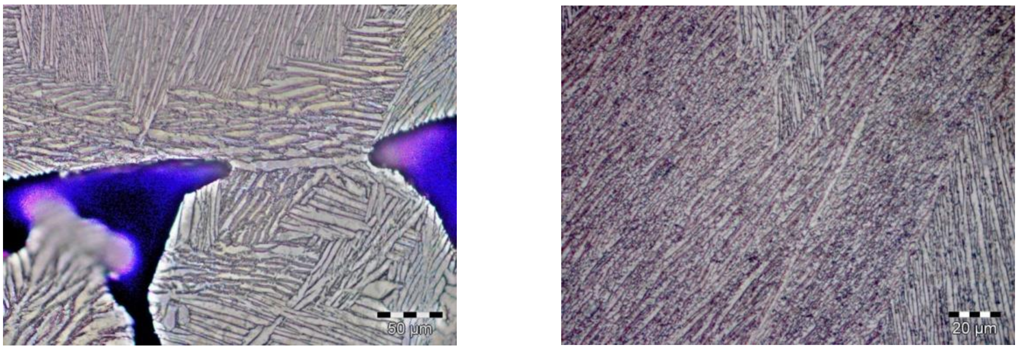
The microstructure presented in Fig. 13 a. through d. is a typical basket weave or Widmanstätten. To note are the various α plate thickness present in various regions of the implant: in the compact region fine and narrow α plates are observable (Fig. 13 c. upper region of the micrograph and Fig. 13. d) while in the porous region thicker plates (Fig. 13. c the circular section) appear.

Measuring the lamellae thickness resulted in a mean value of 2.32±0.58µm in the compact region and 4.33±1.09µm in the porous region. The thickness variation is explained by different cooling rates – higher in the compact and intermediate – low in the porous region.



a.

b.



c. d.

Fig. 13 Fully lamellar microstructures in a Ti-6Al-4V acetabular cup, a. microstructure on compact and porous regions, b. lamellae thickness depending on cooling rate with higher magnification detail in c., and d. lamellae thickness in compact region

Bi-modal structures appear post thermo-mechanical processing below β transus, hot working being performed in α+β phase field where α lamellae are plastically deformed without breakage followed by aging/stress relieving [10, 13]. Factors of influence on the microstructure are the recrystallization annealing temperature which determines α grain size and volume fraction and cooling rate which influences α lamellae thickness.

To illustrate this type of microstructure metallographic specimens were obtained from a Ti-6Al-4V centromedullary nail (shown in Fig. 14) from two regions with various thicknesses.

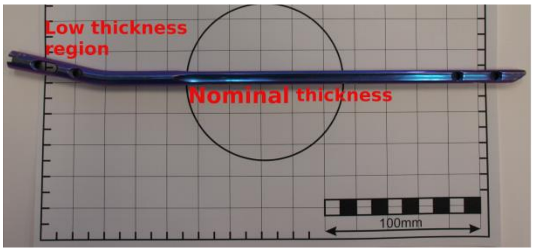
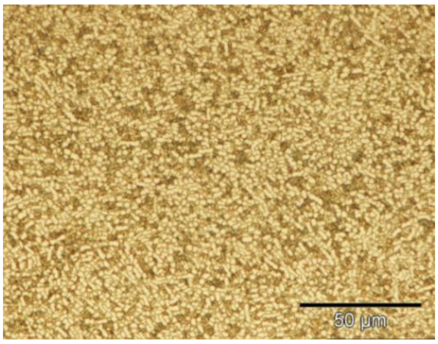


Fig. 14 Centro-medullar nail showing thickness variation

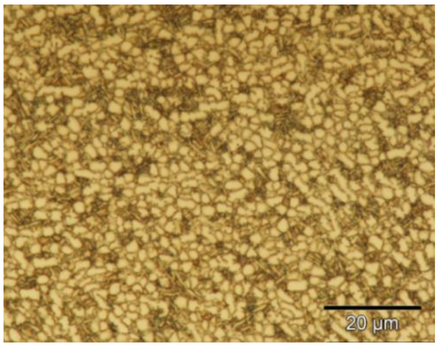
Plastic deformation in α+β phase field yielded a lamellar α plate deformed and oriented microstructure, shown in Fig. 15 a. and b.

Different cooling rates conditioned by implant thickness created the premises for a bi-modal structure, shown in Fig. 16 a. and b.

The previous deformed lamellar α changed its appearance towards an equiaxed morphology in a lamellar α+β matrix [22, 57-61]. The microstructure variation caused by section thickness can create deleterious mechanical characteristics variations.



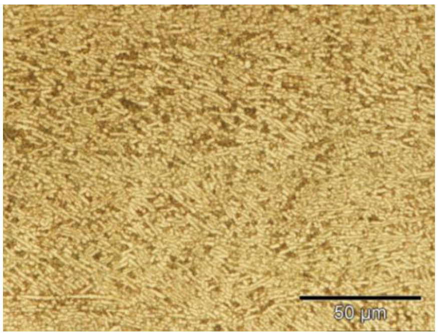
a.



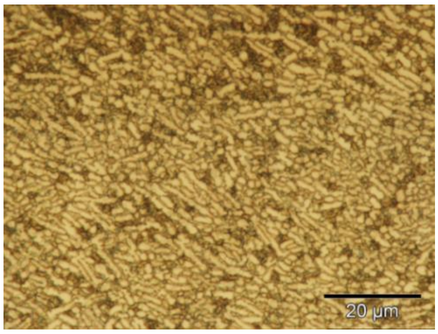
b.

Fig. 15 Microstructure of a Ti-6Al-4V. Sample obtained from centro-medullar nail in a nominal thickness section, a. bimodal microstructure and b. detail showing α and β morphology.

The β titanium alloys have in their chemical composition sufficient β stabilizers to suppress the martensitic transformation, the whole structure being β. In general, the processing route of β alloys comprises hot working in α+β phase field and heat treatment: solution annealing, quenching and aging. Solution heat treatment performed above β transus will generate a coarse microstructure, grain size being controlled by proper temperature selection and successive deformations and recrystallization.



a.



b.

Fig. 16 Microstructure of a Ti-6Al-4V. Sample obtained from centro-medullar nail in a thin section, a. preferred orientation α and b. detail showing β distribution between α.

The α phase can precipitate on grain boundary, an unwanted aspect which can be avoided by rapid cooling. When aged α precipitates as fine platelets with strengthening effect.

The dependency microstructure – mechanical properties (tensile, fatigue, toughness) is known, an aspect which dictates its use for certain applications.

Commercially Pure Titanium and α are mainly used in applications where corrosion resistance is of highest importance. Their mechanical strength is adequate for orthopedic applications, but the low fatigue strength limits their applicability. Small amount of information is available regarding fatigue of titanium and α alloys in medical devices.

When fatigue and mechanical strength are important higher strength titanium are used: in near α alloys the retained β acts as a ductile inclusion arresting crack growth. In α+β alloys the phase mixture increases mechanical strength. When compared to α alloys where adjacent grains are similar, in α+β alloys the α/β interface is a region of strain accumulation which stops slip transmission.

Fully lamellar microstructures owe their good characteristics to α colony size, when a colony equals the size of an individual plate the characteristics are improved. Bi-modal structures are influenced by grain size; smaller grains ensure higher mechanical characteristics and good ductility.

4. Conclusion

Controlling microstructure using processing parameters (temperatures, cooling rates and deformation degree) appears a simple task, but given the complex geometry of medical implants proves harder than expected. Various sections with various thicknesses alter especially cooling rates creating premises for unwanted features, different microstructure appearing in the implant which can be deleterious in most applications resulting in catastrophic failure and sometimes beneficial when rigidity is to be controlled.

R E F E R E N C E S

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