

Title of the lesson: Titanium and Ti-alloys

Title of the MSc subject: Materials Science

Author of the lecture notes: Zsoldos Ibolya

TITANIUM AND Ti-ALLOYS

1. STRUCTURE AND PROPERTIES

The Titanes (Titans) were six Greek gods, sons of Uranus (the god of the Sky) and Gaia (the goddess of the Earth), who were known about their extremely huge strength.

The chemical element of titanium was called by the Titanes, and this name has reality according to the properties of the titanium.

Titanium is lightweight, strong, corrosion resistant and abundant in nature. Titanium and its alloys possess tensile strengths from 210 to 1380 MPa, which are equivalent to those strengths found in most of alloy steels. The density of titanium is only 56 percent that of steel, and its corrosion resistance compares well with that of platinum. Of all the elements in the earth's crust, titanium is the ninth most plentiful.

Titanium has a high melting point 1725°C. This melting point is approximately 220°C above the melting point of steel and approximately 1100°C above that of aluminium.

Titanium extraction

Although titanium is the fourth most common metal elements in the earth's crust (behind aluminium, iron, and magnesium), production of titanium metal is extremely sensitive to contamination, particularly by oxygen, which accounts for its relatively recent development and high cost.

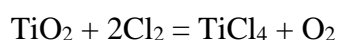
The main ores used in the primary production of titanium are ilmenite, which accounts for about 90% of production, and rutile, which accounts for the remaining 10%. Both types of these ores contain TiO₂ together with more or less contaminants.

Titanium can't be extracted by reducing the ore using carbon as a cheap reducing agent. The problem is that titanium forms a carbide, TiC, if it is heated with carbon, so we don't get the pure metal that we need. The presence of the carbide makes the metal very brittle. That means that we have to use an alternative reducing agent. In the case of titanium, the reducing agent is either sodium or magnesium. Both of these would, of course, first have to be extracted from their ores by expensive processes.

The ore of the titanium is first converted into titanium tetrachloride, which is then reduced to titanium using either magnesium or sodium:

- **Conversion of TiO₂ into TiCl₄:** the ore rutile (impure titanium dioxide) is heated with chlorine and coke at a temperature of about 1000°C.

The chemical reaction is:

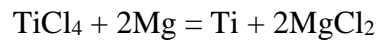


Other metal chlorides are formed as well because of other metal compounds in the ore. Very pure liquid titanium tetrachloride can be separated from the other chlorides by fractional distillation under an argon or nitrogen atmosphere, and is stored in totally dry tanks.

- **Reduction of the titanium tetrachloride:** TiCl_4 can be reduced using either magnesium or sodium.

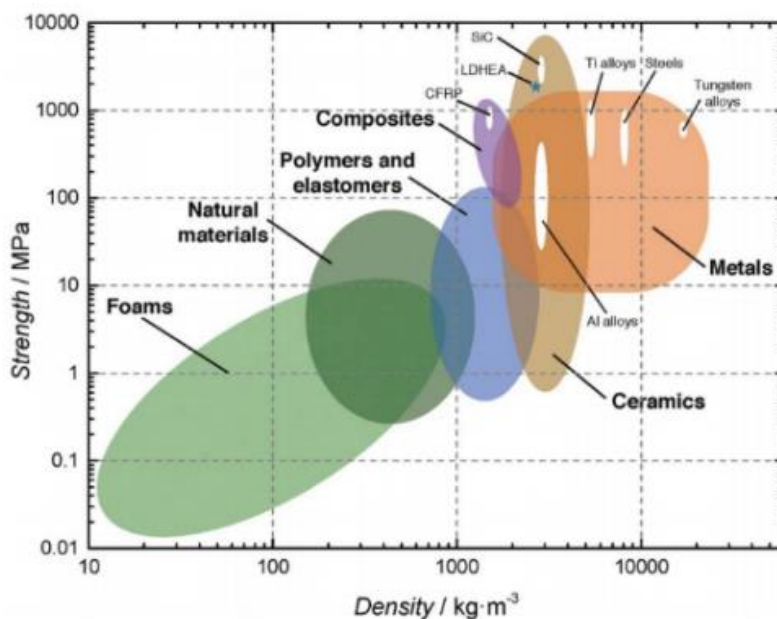
Titanium tetrachloride vapour is passed into a reaction vessel containing molten magnesium in an argon atmosphere, and the temperature is increased to about 1000°C . The reduction process is very slow, taking about 2 days, followed by several more days of cooling.

The chemical reaction is:



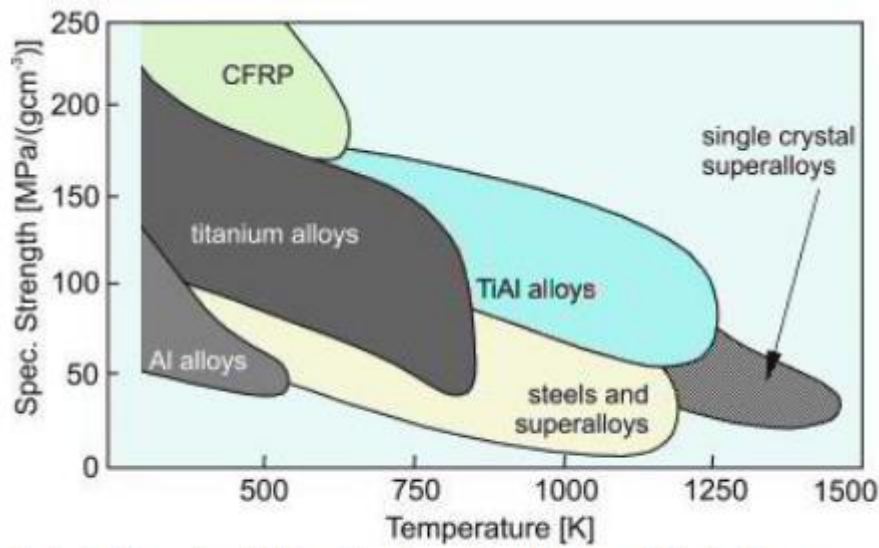
All the magnesium chloride dissolves in the water present, and the remaining titanium is processed further to purify it.

In Figure 1-2 comparisons of strength, density and heat resistant properties of different materials families can be seen. In general, it can be said that titanium alloys are applicable in case of such parts where high strength and low density are required at high temperature.



Ashby plot of strength vs. density for engineering materials. Credit: Elsevier 2010 / Khaled M. Youssef et. al.

Figure 1: Plot of strength vs. density for different engineering materials families.



Mechanical Properties of Titanium Alloys (image from: Titanium and Titanium Alloys. Fundamentals and Applications. eds. Leyens, Peters)

Figure 2: Specific strengths at different temperatures in case of Ti-alloys and some other reference engineering materials.

The world production of titanium is very small, hundreds of thousands of tonnes, which really is small, compared to steel at 800 million tonnes per annum (Table 1). 80% of all the titanium produced is used in the aerospace industries. Car suspension springs could easily be made of titanium with a great reduction in weight but titanium is not available in the large quantities needed and certainly not at the price required for automobile applications. The target price for titanium needs to be reduced to about 30% of its current value for serious application in mass-market cars.

Pure titanium has excellent resistance to corrosion and is used widely in the chemical industries. There is a passive oxide film, which makes it particularly resistant to corrosion in oxidising solutions. The corrosion resistance can be further improved by adding palladium (0.15 wt%).

Table 1: Some properties of commercially pure metals

	Mg	Al	Ti	Fe
Density / g cm ⁻³	1.74	2.7	4.51	7.87
Modulus / GPa	45	70	120	210
Specific Modulus / GPa cm ³ g ⁻¹	25.9	26	26	27
Melting Temperature / °C	650	660	1670	1535
Crystal Structure (300 K)	h.c.p.	c.c.p.	c.p.h.	Cubic-I
Production per annum /tonnes	5 × 10 ⁵	2 × 10 ⁷	5 × 10 ⁵	8 × 10 ⁸
Energy Cost / MW h tonne ⁻¹	??	70	130	15
Relative Cost	7.5	3.7	9	1.0

The crystal structure of titanium at ambient temperature and pressure is close-packed hexagonal (α) with a c/a ratio of 1.587. At about 890°C, the titanium undergoes an allotropic transformation to a body-centred cubic β phase, which remains stable to the melting temperature.

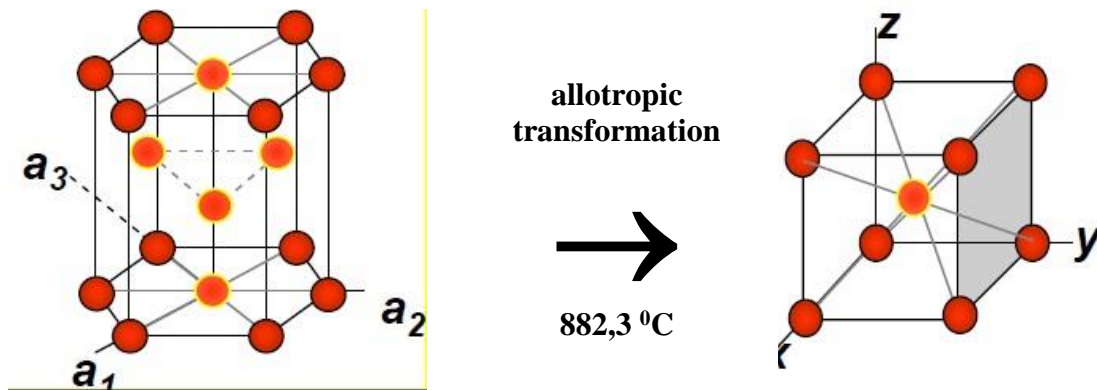


Figure 3: $\alpha \rightarrow \beta$ allotropic transformation

2. ALLOYING ELEMENTS OF TITANIUM

The alloying elements can be categorised according to their effect on the stabilities of the α and β phases (Figure 4). Thus, Al, O, N and Ga are all α -stabilisers. Mo, V, W and Ta are all β -stabilisers. Cu, Mn, Fe, Ni, Co and H are also β -stabilisers but form the eutectoid. The eutectoid reaction is frequently sluggish (since substitutional atoms involved) and is suppressed. Molybdenum and vanadium have the largest influence on β -stability and are common alloying elements. Tungsten is rarely added due to its high density. Cu forms TiCu_2 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.

α -Stabilisers

α -stabilisers are more soluble in the α -phase and raise the β transus temperature.

Figure 4.a typifies the binary phase diagram formed by addition of an α -stabiliser (such as aluminium, oxygen, nitrogen or carbon) to titanium. Oxygen is added to pure titanium to produce a range of grades having increasing strength as the oxygen level is raised. Aluminium is the only other α -stabiliser used commercially and is a major constituent of most commercial alloys. It is a very effective α -strengthening element at ambient and elevated temperatures up to about 550°C. The low density of aluminium is an additional advantageous feature but the amount that can be added is limited because of the formation of a brittle titanium-aluminium compound at aluminium contents exceeding about 8% by weight.

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The α -phase is also strengthened by the addition of tin (Sn) or zirconium (Zr). These metals have appreciable solubility in both α - and β -phases and as their addition does not markedly influence the transformation temperature they are normally classified as **neutral additions**. As with aluminium, the beneficial ambient temperature hardening effect of tin and zirconium is retained at elevated temperatures. Figure 4.b demonstrates schematically the phase diagram for titanium and a neutral element.

β -Stabilisers

Elements that depress the transformation temperature, readily dissolve in and strengthen the β -phase and exhibit low α -phase solubility are known as β -stabilisers. They can be divided into two categories according to their constitutional behaviour with titanium:

- β -isomorphous elements,
- β -eutectoid elements.

β -Isomorphous Elements

β -isomorphous elements exhibit complete mutual solubility with β -titanium. Increasing addition of the solute element progressively depresses the transformation temperature to give the characteristic phase diagram shown in Figure 4.c. Molybdenum and vanadium are the most important β -isomorphous elements, while niobium and tantalum have also found application in some alloys.

β -Eutectoid Elements

β -eutectoid elements have restricted solubility in beta titanium and form intermetallic compounds by eutectoid decomposition of the β -phase. A representative phase diagram is illustrated in Figure 4.d. Elements of the β -eutectoid type can be further subdivided into sluggish and active elements. Commercially important metals in the sluggish category are iron, chromium and manganese. Eutectoid decomposition of β -phase in the titanium-iron, titanium-chromium and titanium-manganese systems is so slow that intermetallic compound formation does not occur during normal commercial fabrication and heat treatment or during service and, therefore, for practical purposes the behaviour of iron, chromium and manganese can be likened to that of β -isomorphous elements.

In contrast, copper and silicon form active eutectoid systems where below the eutectoid temperature the β -phase decomposes to α and intermetallic compounds within commercially acceptable times. As a result, controlled precipitation of the intermetallic compounds can be utilised to enhance the strength of titanium alloys containing appropriate concentrations of silicon or copper.

In addition to strengthening the β -phase, β -stabilisers have two other important advantages as alloying constituents. β -titanium has an inherently lower resistance to deformation than the α -modification and therefore elements which increase and stabilise the β -phase tend to improve alloy fabricability during both hot and cold working operations. Addition of sufficient β -stabiliser to titanium compositions also confers a heat treatment capability which permits

significant strengthening to be achieved by controlled decomposition of β -phase to α -phase during the heat treatment process.

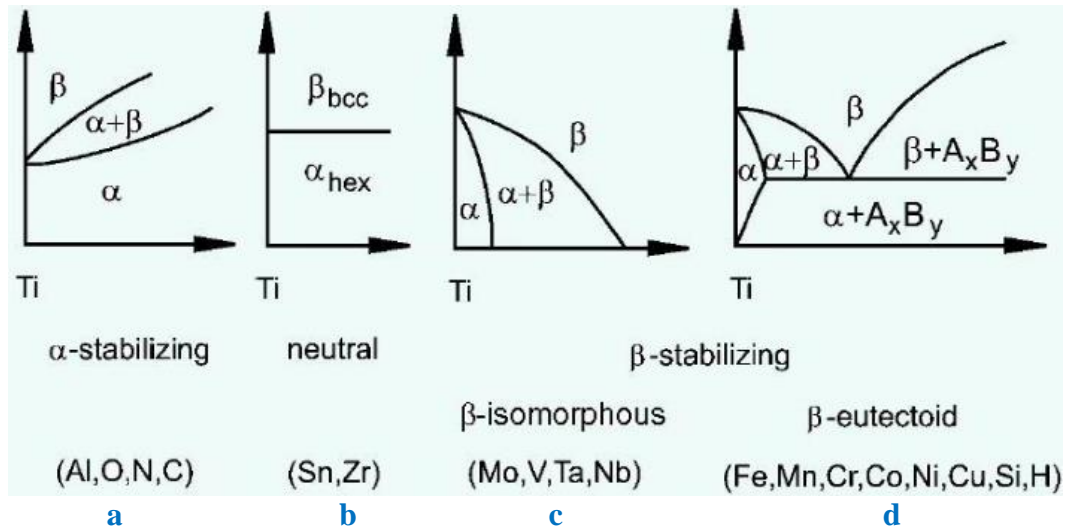


Figure 4: Alloy effects in Ti alloys (Source: <http://www.dierk-raabe.com/titanium-alloys>)

3. Ti-ALLOYS AND THEIR HEAT TREATMENT

There are three structural types of titanium alloys:

- **Alpha Ti-alloys** generally are non-heat treatable, weldable, common properties are: medium strength, good creep strength, good corrosion resistance.
- **Alpha-Beta Ti-alloys** are heat treatable, common properties are: good forming properties, medium to high strength, good creep strength.
- **Beta Ti-alloys** are heat treatable and readily formable, common properties are: very high strength, low ductility.

3.1. Alpha-titanium alloys

Alpha-titanium alloys have further three sub-types:

- commercially pure (CP) titanium-,
- α - and
- near alpha titanium alloys.

3.1.1. Commercially pure (CP) titanium alloys

The total amount of the alloying elements of the CP Ti-alloys is between 0.1-1%. They contain only α -stable alloying elements, mainly oxygen which improve the strength, and the other elements present impurities. Consequently, their microstructure consists of only grains of α -solid solution, Figure 5.a. Their strength is medium high and so this group is the less expensive type of the Ti-alloy family. However, their corrosion resistance to nitric acid, moist chlorine is outstanding. 0.2% Pd addition extends the corrosion resistance in hydrochloric acid (HCl), sulphuric acid (H₂SO₄) and phosphoric acid (H₃PO₄), as well. This type of the Ti-alloys is applied as the material of airframes, heat exchangers, chemicals, marine, surgical implants, Figure 5. b-c.

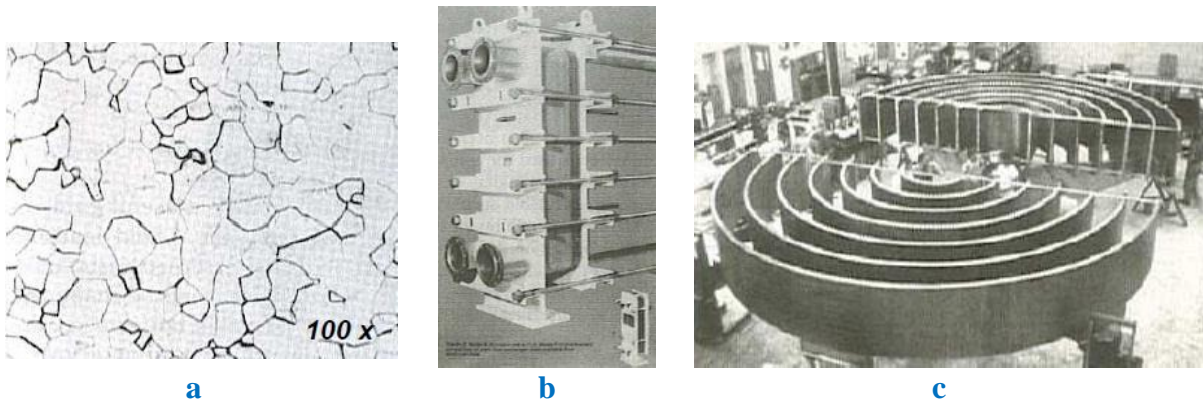


Figure 5: a: HCP α phase structure, b: Plate and frame heat exchanger, c: Large structure used in bleaching section of pulp and paper

Heat treatment of the CP-Ti alloys

After annealing from the β -field (cooling with normal rate) an α -phase having hexagonal crystal structure develops, Figure 6.a.

After quenching from the β -field (rapid cooling) also martensite phase (α' - phase) develops near the α -phase, Figure 6.b-c. Martensite phase means a supersaturated solid solution in case of the Ti-alloys, as well. This martensite phase is stable (in time) at room temperature, however the strength increase is much smaller than for martensite phase of the steels.

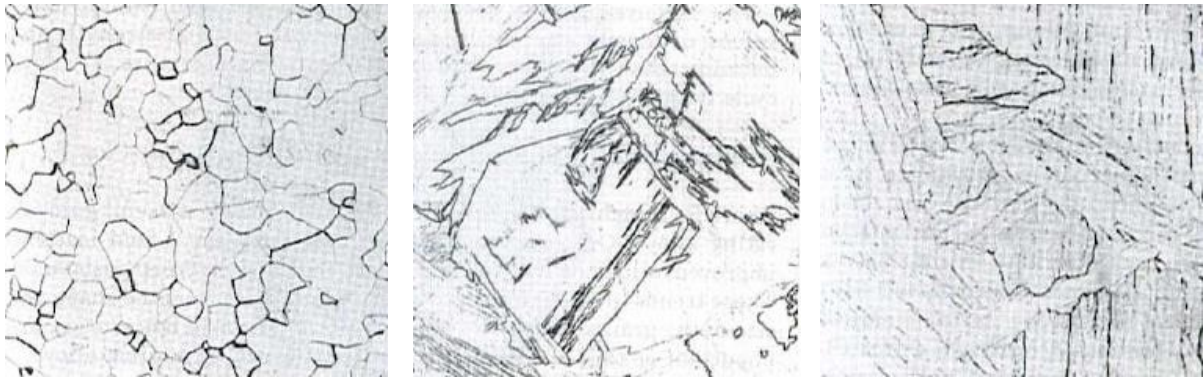


Figure 6: a: Annealed structure. b: Quenched from β -field. c: Air-cooled from β -field.

3.1.2. α -titanium alloys

The α -titanium alloys contain only α -stable alloying elements, as well.

The total amount of the alloying elements of the α -Ti-alloys is between 1-9%. The amount of α stabilisers should not exceed 9% to prevent embrittlement. Al is the main alloying element, which provides solid solution strengthening. O and N present as impurities give interstitial hardening. 5-6% Al can lead to a finely dispersed, ordered phase - α_2 -phase - which is coherent to lattice. α_2 -phase is advantageous in the microstructure regarding the strength, but it is deleterious regarding the ductility. Figure 7 shows the appearance (in the phase diagram) and the characteristic pattern of the α_2 -phase. In the microscopic image the fine precipitations of the chemical compound of Ti_3Al (white colour) can be seen clearly. Sn (tin, stannum) and Zr (zirconium) are also added in small amount to stabilise the α -phase and improve the strength.

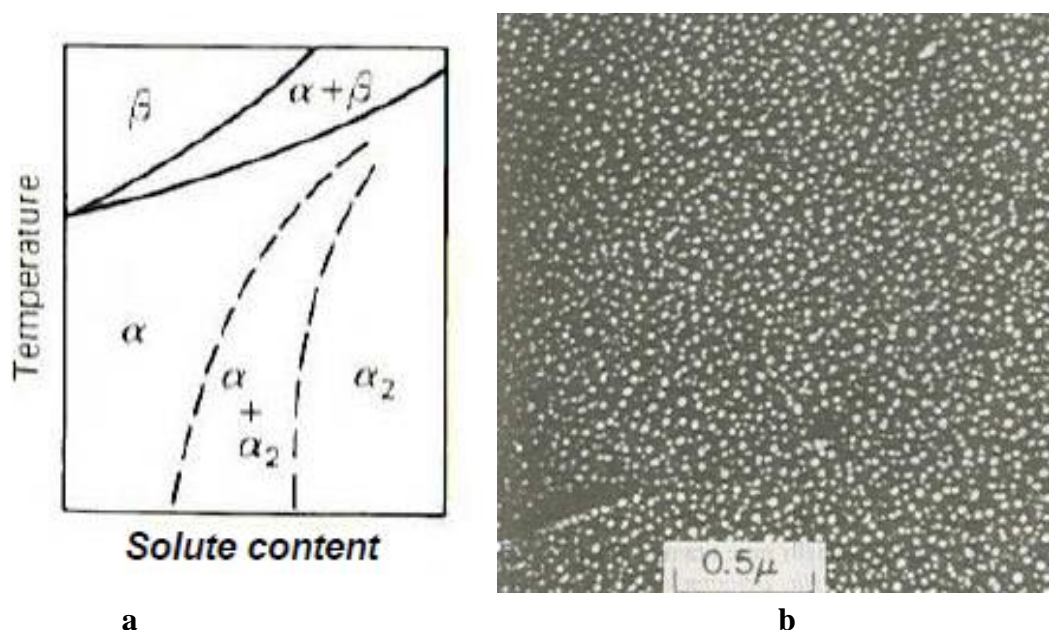


Figure 7: a: Part of the Ti-Al phase diagram b: Microstructure of the α_2 -phase.

Heat treatment of the α -Ti alloys

The possibilities and the heat treatment cases are the same as for CP Ti alloys. Also, parallel with the appearance of the α_2 -phase an additional strengthening can be reached by quenching and forming martensite phase in the structure, Figure 6.

α -titanium alloys have a moderate strength which depend on the Al and/or O contents. The aluminium reduces the density, as well. These alloys are readily weldable, they have a good oxidation resistance upto 600 °C. Aircraft engine compressor blades, sheet-metal parts are characteristic in the applications, however, material of cryogenic vessels used at -250 °C are these alloys, as well.

3.1.3. Near α -titanium alloys

Near the α -stabilisers, the so called „near α -Ti alloys” contain a smaller amount of β -stabilisers (1-2%). The amount of the α -stabilisers is larger than for CP and α -Ti alloys, in order to keep the good ductility. As β -stabilisers molybdenum and vanadium are used, so these alloys become heat treatable to β -phase, as well.

Heat treatment of the near α -Ti alloys

Two essential types of the heat treatment are applied.

The first type is a **heat treatment from lower temperature**. The alloy is heated to the $\alpha+\beta$ field, to „T” in Figure 8, where the alloy obtains around equal amount of α and β phases.

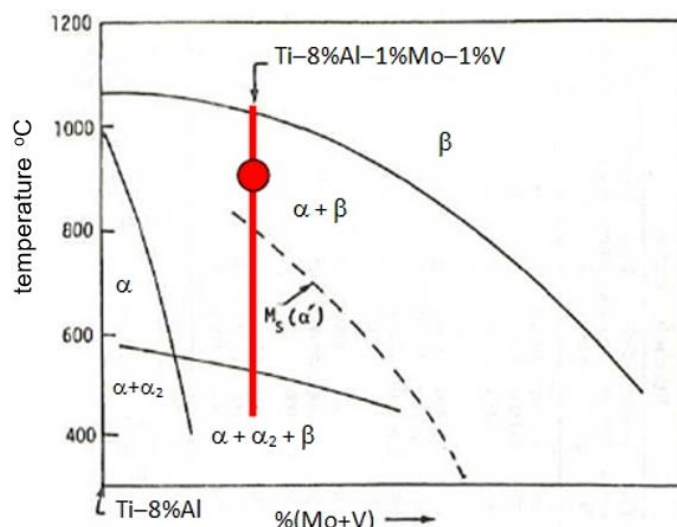


Figure 8: Pseudo-binary diagram for Ti-8%Al with Mo and V addition

Air-cooling gives primary α -phase and Widmanstätten α formed by nucleation and growth from the β -phase, Figure 9. In case of faster cooling the β transforms into martensitic α' which gives higher strength.



Figure 9: Air-cooled from $\alpha+\beta$ phase field, having white primary α -phase and Widmanstätten α - β structure

The second type is a **heat treatment from higher temperature**: the alloy is heated to the β field. Quenching from the β -phase field produces laths of martensitic α' , which are delineated by thin films of β -phase, Figure 10.a. Air-cooling from the β -phase field gives a basket weave structure of Widmanstätten α -phase delineated by β -phase, Figure 10.b.



Figure 10: **a:** Near α -Ti alloy quenched from β -phase field, **b:** Near α -Ti alloy air-cooled from β -phase field

The lamellar structure becomes finer with the increasing of the cooling rate, Figure 11.

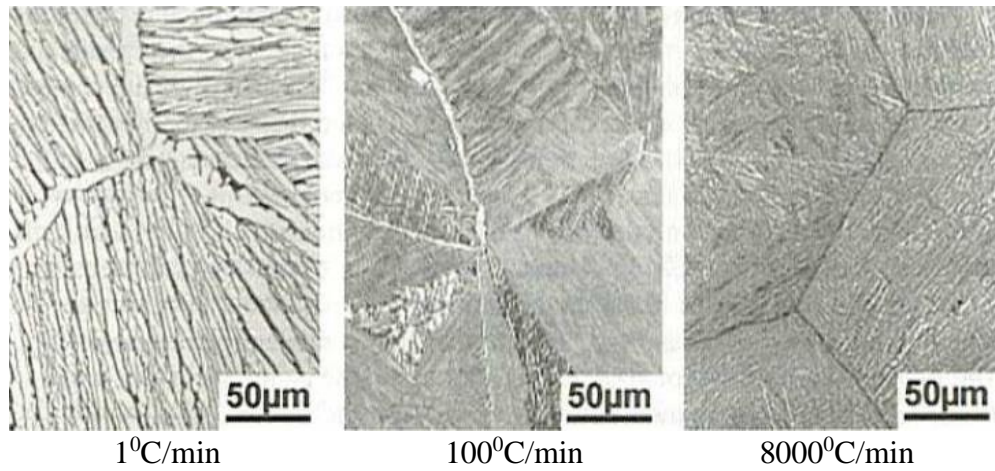


Figure 10: Effects of cooling rate from the beta phase field on lamellar microstructure in near α -Ti alloy

Properties of the near α -Ti alloys

- Moderately high strength at room temperature and relatively good ductility (~15%).
- High toughness and good creep strength at high temperatures.
- Good weldability.
- Good resistance to salt-water environment.

Characteristic examples of the near α -Ti alloys, Ti-8Al-1Mo-1V és a Ti-6Al-2Sn-4Zr-Mo alloys are applied in airframe and jet-engine parts requiring high strength at 450 °C, good creep and toughness.

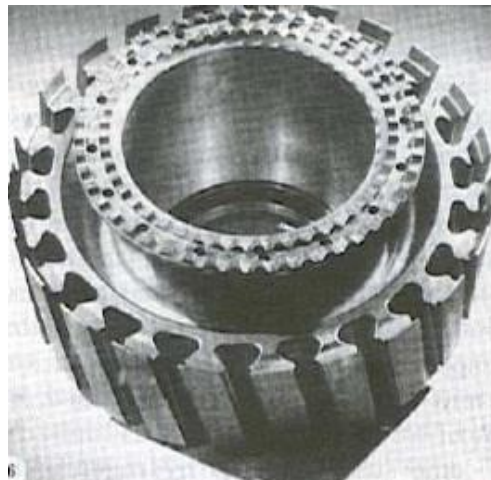


Figure 11: Forged compressor disc made from near α -Ti alloy

3.2. Alpha-Beta Ti-alloys

Alpha-beta titanium alloys contain both of α - and β -phase. α -stabilisers are used with 4-6%. β -stabilisers (3-4%) are used to allow the β -phase to retain at room temperature after quenching from β or $\alpha+\beta$ phase field. Improved strength and formability are characteristic in comparison to α -Ti alloys. Ti-6Al-4V is the most widely commercially used type.

Heat treatment of the α - β -Ti alloys

The heat treatment processes are studied in the example of the Ti-6Al-4V in this lesson. The view of the developed microstructure after different heat treatment processes of casted Ti-6Al-4V is being shown schematically in Figure 12.

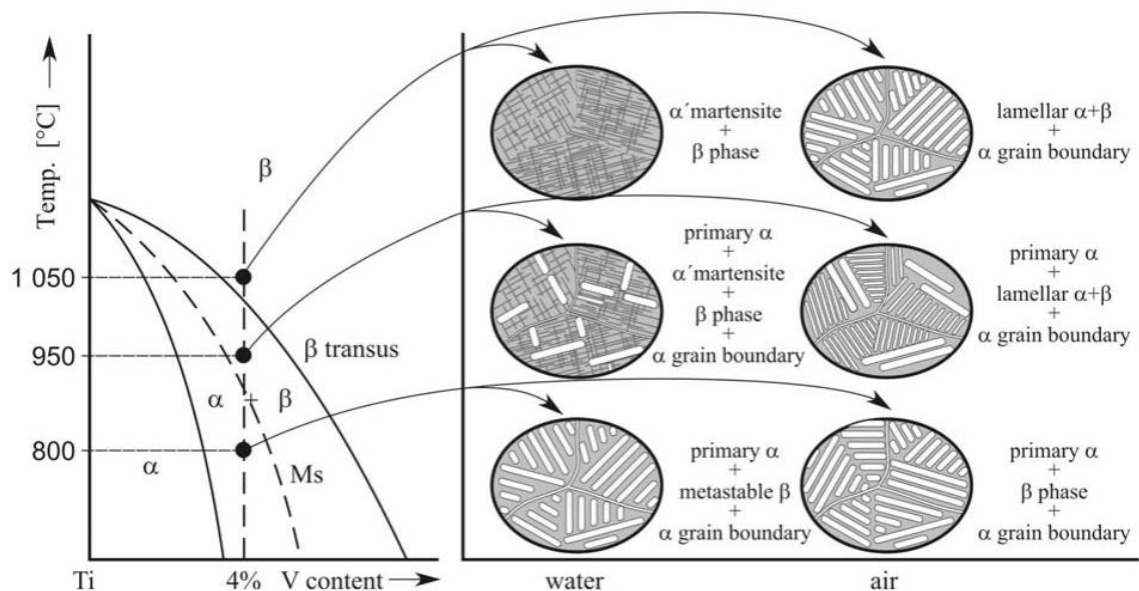


Figure 12: Schematic representation of microstructures developed after solution treatment of casted Ti-6Al-4V titanium alloy

The microstructure of **as-cast** Ti6Al4V alloy is shown in Figure 13. The structure of the alloy is two-phased, consists of α and β solid solutions. The lamellae of the α -phase (light) are relatively regular and are mutually connected in a form of basket weave. Between these phases are thin areas of β -phases (dark). By the boundaries of the prior β -grains α -phase was formed which "delimits" these grains (grain boundary α).

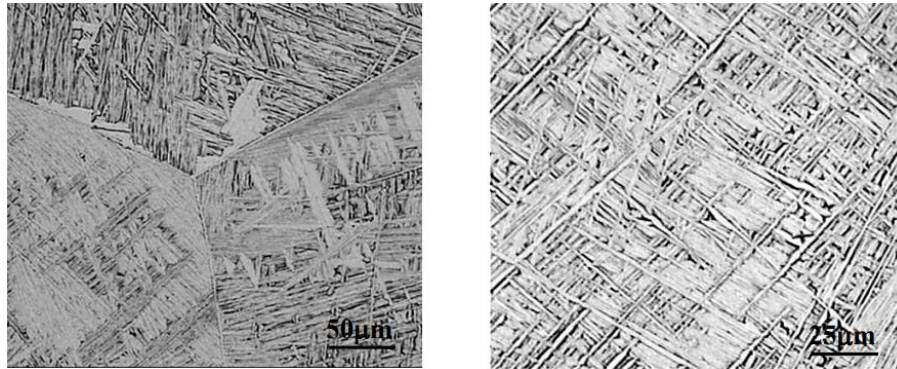


Figure 13: Microstructure of as-cast Ti6Al4V alloy in different magnification

The microstructures after the heat treatment **from the β -field** (1050 °C) are shown in the Figure 14. As a result of fast cooling in water an acicular (needle-shaped) α' martensite structure was formed. Following the fast cooling from 1050 °C no deposition of grain boundary α can be recognized, Fig. 14.a. Heat treatment at 1050 °C by air cooling leads to the typical lamellar $\alpha + \beta$ structure with a grain boundary α on the prior β grains, Fig. 14.b.

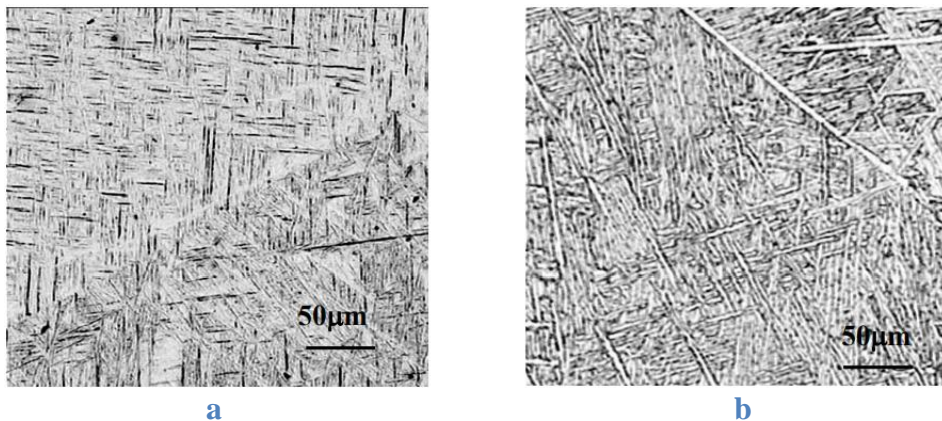


Figure 14: Microstructures after heat treatment from the β -field of Ti6Al4V alloy. **a:** water-cooling, **b:** air-cooling

Cooling in water **from the $\alpha + \beta$ -field** (950 °C) produces a microstructure which consist of acicular α' martensite and primary α -phase, Figure 15.a. On the borders of prior β grains an α grain boundary are formed. The microstructure of Ti-6Al-4V alloy after the heat treatment, with air-cooling from 950 °C/air is shown in Figure 15.b. The structure contains a lamellar mixture of $\alpha + \beta$ phases, primary α -phase and grain boundary α . Considering the low cooling rate no α' martensite is formed.

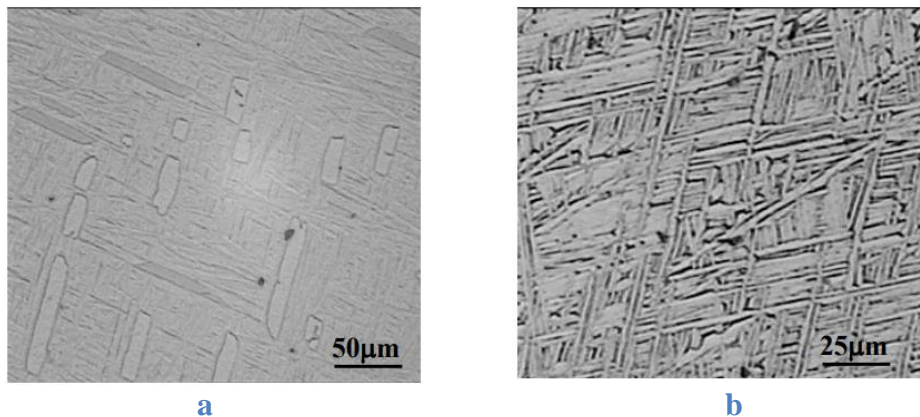


Figure 15: Microstructures after heat treatment from the $\alpha + \beta$ -field of Ti-6Al-4V alloy. **a:** water-cooling, **b:** air-cooling

Properties of the α - β -Ti alloys

Ti-6Al-4V is the most widely used titanium alloy. It features good machinability and excellent mechanical properties. The Ti-6Al-4V alloy offers the best all-round performance for a variety of weight reduction applications in aerospace, automotive and marine equipment. Ti-6Al-4V also has numerous applications in the medical industry. Biocompatibility of Ti-6Al-4V is excellent, especially when direct contact with tissue or bone is required.

Ti-6Al-4V is typically used for:

- Direct Manufacturing of parts and prototypes for racing and aerospace industry,
- Biomechanical applications, such as implants and prosthesis,
- Marine applications,
- Chemical industry,
- Gas turbines.

3.2. Beta Ti-alloys

Beta stabilisers are sufficiently added to retain a **fully β -structure** (avoid martensite formation) when quenched from the β -phase field. In Figure 16 the conditions of the metastable and stable formations of β -alloys are shown.

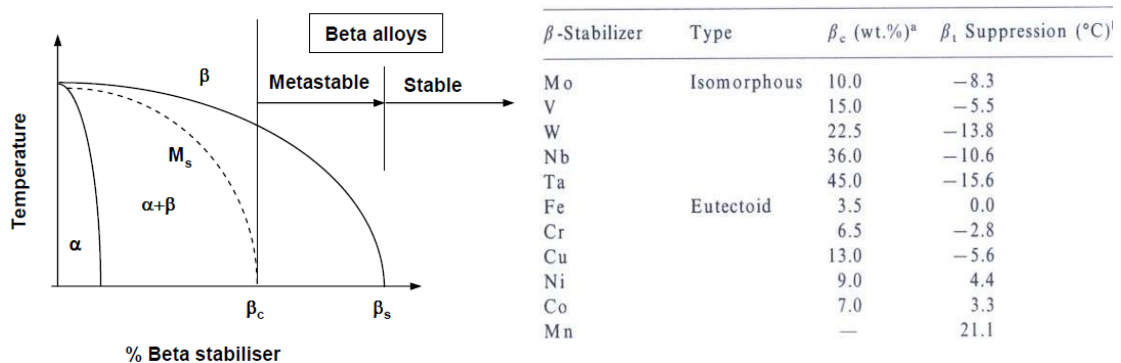


Figure 16: Metastable and stable formations of β -alloys

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Metastable β -structures (in full volume) can be produced by rapid cooling while stable β -structures (in full volume) remain after a simple air-cooling (steady, equilibrium cooling, leaving alone the alloy) at room temperature.

The limits of these two types are given in the molybdenum equivalent, whose definition is:

$$Mo_{equiv} \% = 1.0Mo + 0.67V + 0.44W - 0.28Nb + 0.22Ta + 1.6Cr + \dots - 1.0Al$$

The limits for the metastable and stable cases are:

- Metastable β -alloys : $Mo_{equiv} < 25$,
- Stable β -alloys : Mo_{equiv} : 25-40.

β -Ti alloys possess a BCC crystal structure, which is readily cold-worked (better than HCP α structure) in the β -phase field. The microstructure after quenching contains equiaxed β -phase, Figure 17. After solution heat treating + quenching a very high strength (up to 1300-1400 MPa) can be reached.

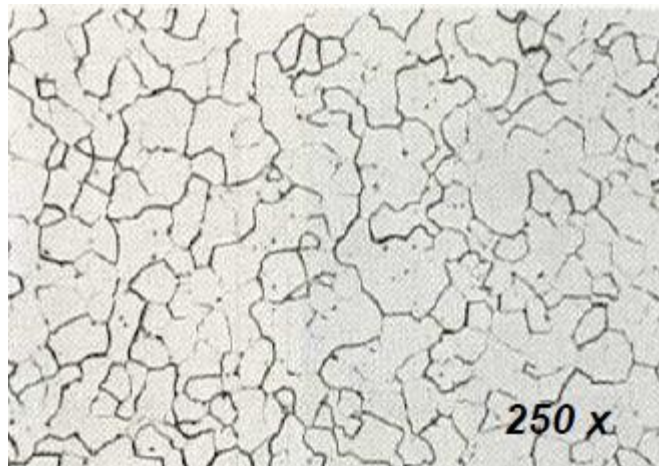


Figure 17: Ti-13V-11Cr-3Al alloy solution heat-treated and water-quenched

Metastable β -Ti alloys are hardenable while stable β -Ti alloys are non-hardenable.

Most β -titanium alloys are metastable and tend to transform into:

- coarse α -plates after heat-treated in the $\alpha+\beta$ phase field or
- α -phase precipitation after long-term ageing at elevated temperature.

This effect gives higher strength to the alloy but can cause embrittlement which is not desirable when ductility is required.

A more detailed classification of the Ti-alloys containing β -stabiliser alloying element(s) can be seen in Figure 18. It has to be mentioned that the production and heat treatment of the β -Ti alloys and α - β -Ti alloys need especially great care, because there are undesirable (harmful) phases (e.g. the ω -phase) whose existence can destroy the good properties which were achieved by the previous, expensive technologies, therefore their formation has to be avoided.

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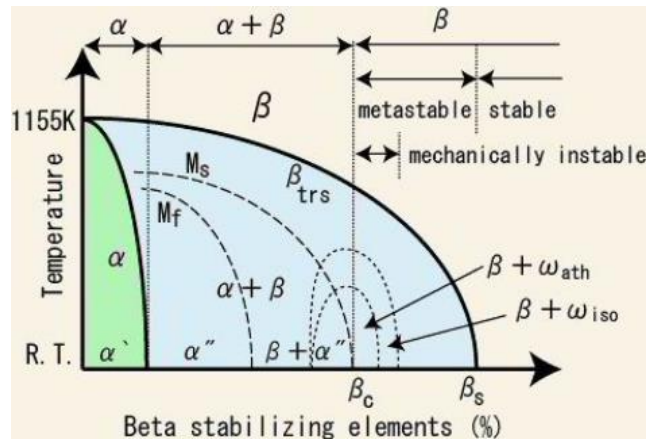


Figure 18: Classification of Ti-alloys containing β -stabiliser alloying elements

In the following tables different types, properties, applications, advantages and disadvantages of the β -Ti alloys are summarised.

Alloy composition	Commercial name	Category (Mo equivalent)	T_{β} ($^{\circ}\text{C}$)	Actual and potential applications	Year introduced (company)
Ti-35V-15Cr	Alloy C	Beta (47)		Burn resistant alloy	1990 (P&W)
Ti-40Mo		Beta (40)		Corrosion resistance	1952 (RemCru)
Ti-30Mo		Beta (30)		Corrosion resistance	1952 (RemCru)
Ti-6V-6Mo-5.7Fe-2.7Al	TIMETAL 125	Metastab (24)	704	High strength aircraft fasteners	1990 (TIMET)
Ti-13V-11Cr-3Al	B120 VCA	Metastab (23)	650	Airframe, landing gear, springs	1952 (RemCru)
Ti-1Al-8V-5Fe	1-8-5	Metastab (19)	825	Fasteners	1957 (RMI)
Ti-12Mo-6Zr-2Fe	TMZF	Metastab (18)	743	Orthopedic implants	1992 (Howmedica)
Ti-4.5Fe-6.8Mo-1.5Al	TIMETAL LCB	Metastab (18)	800	Low cost, high strength alloy	1990 (TIMET)
Ti-15V-3Cr-1Mo-.5Nb-3Al-3Sn-.5Zr	VT35	Metastab (16)		High strength airframe castings	n.a. (Russian)
Ti-3Al-8V-6Cr-4Mo-4Zr	Beta-C	Metastab (16)	795	Oil-fields, springs, fasteners	1969 (RMI)
Ti-15Mo	IMI 205	Metastab (15)	727	Corrosion resistance	1958 (IMI)
Ti-8V-8Mo-2Fe-3Al	8-8-2-3	Metastab (15)	775	High strength forgings	1969 (TIMET)
Ti-15Mo-2.6Nb-3Al-0.2Si	Beta 21S	Metastab (13)	807	Oxidation/corrosion resist, MMC	1989 (TIMET)
Ti-15V-3Cr-3Sn-3Al	15-3	Metastab (12)	760	Sheet, plate airframe castings	1978 (USAF)
Ti-11.5Mo-6Zr-4.5Sn	Beta III	Metastab (12)	745	High strength	1969 (Crucible)
Ti-10V-2Fe-3Al	10-2-3	Metastab (9.5)	800	High strength forgings	1971 (TIMET)
Ti-5V-5Mo-1Cr-1Fe-5Al	VT22	Metastab (8)	850	High strength forgings	n.a. (Russian)
Ti-5Al-2Sn-2Zr-4Mo-4Cr	Ti-17	Beta-rich (5.4)	885	High strength, medium temperature	1968 (GEAE)
Ti-4.5Al-3V-2Mo-2Fe	SP700	Beta-rich (5.3)	900	High strength, SPF	1989 (NKK)
Ti-5Al-2Sn-2Cr-4Mo-4Zr-1Fe	Beta CEZ	Beta-rich (5.1)	890	High strength, medium temperature	1990 (CEZUS)
Ti-13Nb-13Zr		Beta-rich (3.6)		Orthopedic implants	1992 (Smith&Neph)

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Advantages and disadvantages of beta titanium alloys

<i>Advantages</i>	<i>Disadvantages</i>
<ul style="list-style-type: none">- high strength-to-density ratio- low modulus- high strength/high toughness- high fatigue strength- good deep hardenability- low forging temperature- strip producible – low-cost TMP* (some alloys)- cold formable (some alloys)- easy to heat treat- excellent corrosion resistance (some alloys)- excellent combustion resistance (some alloys)	<ul style="list-style-type: none">- high density- low modulus- poor low and high temperature properties- small processing window (some alloys)- high formulation cost- segregation problems- high springback- microstructural instabilities- poor corrosion resistance (some alloys)- interstitial pick up

* TMP: thermomechanical processing

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