Chapter 5
Titanium Alloys: Part 1—Physical Metallurgy and Processing

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Abstract Titanium alloys are the principal replacements, and in many cases also prime candidate materials to replace (i) aerospace special and advanced steels, owing to their higher specific strength properties, (ii) aluminium alloys, due to their better elevated temperature properties and (iii) nickel-base superalloys for high pressure compressors of modern engines, owing to their superior intermediate temperature (up to 600 °C) creep strength and excellent oxidation and corrosion resistance and good damage tolerant properties. This chapter summarily presents the chemical compositions, properties, aerospace applications and briefly covers (a) the physical metallurgy of titanium alloys, (b) Primary (Melting and Casting) and Secondary (Processing) processes and (c) alloy development (commercially pure Ti, α, near-α, $\alpha + \beta$ and β alloys). Towards the end, the Indian scenario is presented in terms of available production facilities and some of the indigenous alloys.

Keywords Titanium · Alloys · Physical metallurgy · Primary and secondary processing · Castings

5.1 Introduction

Titanium is present in the earth's crust at a level of about 0.6 % and is therefore the fourth most abundant structural metal after aluminium, iron and magnesium. The most important mineral sources for Ti are ilmenite ($FeTiO_3$) and rutile (TiO_2).

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Table 5.1 Properties of titanium compared with those of the other widely used structural metals Fe, Ni and Al [1]

Attributes	Ti	Fe	Ni	Al
Melting point (°C)	1670	1538	1455	660
Allotropic transformation (°C)	882	912	–	–
Crystal structure	Bcc hex	Bcc hex	Fcc	Fcc
Room temperature E (GPa)	115	190	210	70
Yield stress (MPa)	1000	1000	1000	500
Density (g/cm^3)	4.5	7.9	8.9	2.7
Comparative corrosion resistance	Very high	Low	Medium	High
Comparative reactivity with oxygen	Very high	Low	Low	High
Comparative metal price	Very high	Low	High	Medium

High strength, low density and excellent corrosion resistance are the main properties that make titanium attractive for a variety of applications. Examples include aircraft (high strength in combination with low density), aeroengines (high strength, low density and good creep resistance up to about 600 °C), biomedical devices (corrosion resistance, low modulus compared to Co- and Fe-based alloys and high strength) and components in chemical processing equipment (corrosion resistance). The relatively high cost of titanium has hindered wider use, e.g. in automotive applications, although new fuel economy standards may change this.

Some of the basic characteristics of titanium are compared in Table 5.1 with those of the other major structural metals based on Fe, Ni and Al. Although titanium has the highest strength to density ratio, it is the material of choice only for certain applications because of its high cost, which is mainly due to the requirement of inert atmosphere or vacuum environments during production of titanium sponge from titanium tetrachloride, and also consolidation of the metal. Both processes require high energy consumption.

The high reactivity of titanium with oxygen leads to the immediate formation of a stable and adherent oxide surface layer when exposed to air, resulting in superior corrosion resistance in most aggressive environments, especially aqueous acid environments. However, this high reactivity with oxygen limits titanium alloy usage to about 600 °C. Above this temperature the diffusion of oxygen through the oxide surface layer becomes too fast, resulting in excessive growth of the oxide layer and embrittlement of the oxygen-enriched surface layer of the titanium alloy.

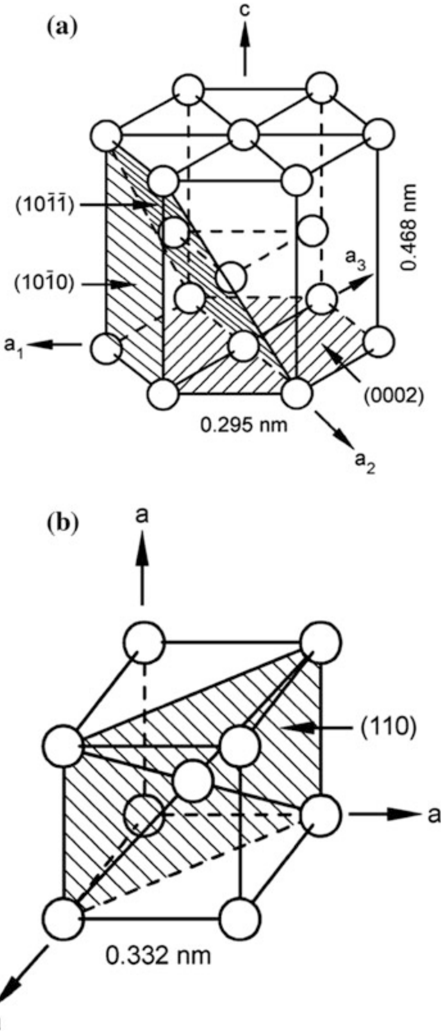
5.2 Physical Metallurgy of Titanium Alloys

5.2.1 Crystal Structure

Pure titanium undergoes an allotropic phase transformation at 882 °C, changing from a body-centred cubic crystal structure (β phase) at higher temperatures to a hexagonal-close-packed crystal structure (α phase) at lower temperatures. The exact transformation temperature is strongly influenced by interstitial and substitutional elements and therefore depends on the composition and purity of the metal.

The hexagonal structure cell of the α phase is shown in Fig. 5.1a, which also indicates the room temperature values of the lattice parameters (a = 0.295 nm and c = 0.468 nm). The resulting c/a ratio for pure α titanium is 1.587, less than the ideal ratio of 1.633 for the hexagonal-close-packed crystal structure. Also indicated in Fig. 5.1a are the three most densely packed lattice planes: the close-packed (0002) plane, also called basal plane; one of the three $\{10\bar{1}0\}$ prism planes; and one

Fig. 5.1 Unit cells of **a** hexagonal-close-packed (HCP) α titanium and **b** body-centred cubic (BCC) β titanium, showing different slip planes [1]



of the six $\{10\bar{1}\bar{1}\}$ pyramidal planes. The three a_1, a_2 and a_3 axes are the close-packed directions with the indices $\langle 11\bar{2}0\rangle$.

The unit cell of the body-centred cubic (bcc) β phase is illustrated in Fig. 5.1b, also indicating one variant of the six most densely, but not close-packed {110} lattice planes and the lattice parameter value of pure β titanium at 900 °C ($a = 0.332$ nm). The close-packed directions in the bcc structure are the six $\langle 111\rangle$ directions.

5.2.2 Elastic Properties

The hexagonal crystal structure of the α phase is intrinsically anisotropic. This anisotropy has important consequences for the elastic and plastic properties of titanium and its alloys. Young's modulus varies with angle of declination from the 'c' axis. Young's modulus of elasticity, E, is about 145 GPa when the stress axis is parallel to the c-axis, and 100 GPa when the stress axis is perpendicular to the c-axis [2].

Similar strong directional variations are observed for the shear modulus, G, of single crystals: G varies between 46 and 34 GPa for shear stresses applied in $\langle 11\bar{2}0\rangle$ directions and on (0002) or $\{10\bar{1}0\}$ planes, respectively. Less pronounced variations in elastic properties are observed in polycrystalline α titanium with crystallographic texture: a typical value for commercially pure (CP) titanium is 105 GPa.

In general, commercial β titanium alloys have lower E values than α and α + β alloys. Typical E values for commercial β alloys are 70–90 GPa in the as-quenched metastable β condition and 100–105 GPa for the annealed α + β condition. Average E values for the commercial α + β alloys are about 115 GPa [3] but depend on the Al content of each alloy.

5.2.3 Deformation Modes

The ductile behaviour of the hexagonal α-phase, especially at low temperatures, results from the activation of twinning deformation modes in addition to slip. These twinning modes are important for the deformation behaviour of CP titanium and for some α titanium alloys. However, twinning is suppressed nearly completely in two-phase α + β alloys by the fine microstructure (small phase dimensions), Al and oxygen content, and the presence of Ti_3Al precipitates. The α + β alloys are quite ductile at low temperatures owing to the fine microstructures and to the presence of the non-basal **c + a** slip mode described later.

The bcc β phase also shows twinning in addition to slip, but the occurrence of twinning in β alloys is limited to the single-phase state and decreases with increasing solute content. In fully heat-treated β alloys, which are hardened by the precipitation of α particles, twinning is completely suppressed. In these alloys twinning might occur during the forming operations prior to ageing. Some commercial β alloys also can form deformation-induced martensite, which further enhances their formability. Formation of this deformation-induced martensite is, however, very sensitive to alloy composition.

5.2.4 Slip Modes

The various slip planes and slip directions for α titanium are indicated in the hexagonal structure cell in Fig. 5.1a. The main slip directions are the three close-packed directions of the type $\langle 11\bar{2}0 \rangle$. The slip planes containing this $\vec{a}$ type of Burgers vector are the (0002) basal plane, the three $\{10\bar{1}0\}$ prism planes and the six $\{10\bar{1}\bar{1}\}$ pyramidal planes. Among these three different types of slip planes together with the possible slip directions there are a total of 12 slip systems, see Table 5.2 [4, 5], but these all have coplanar slip $\langle 11\bar{2}0 \rangle$ directions so do not satisfy the Taylor–Von Mises criterion for deformation of polycrystals. Therefore the **c + a** slip mode is required.

Taking into account the large difference in critical resolved shear stress (CRSS) between **c + a** slip and **a** slip, which was measured for Ti–6.6Al single crystals (Fig. 5.2) [6], the percentage of grains deforming by **c + a** slip will be quite low in α titanium polycrystals without crystallographic texture, because the activation of 'a' slip is easier even for an angle of about 10° between the stress axis and the *c*-axis. The absolute values of the CRSS are strongly dependent on alloy content and on test temperature (see Fig. 5.2). The small differences in CRSS at room temperature between the three types of slip systems with a basal ($\vec{a}$ type) Burgers vector become even smaller with increasing temperature (Fig. 5.2). As shown for binary Ti–V alloys [7], the slip systems in bcc β titanium alloys are {110}, {112} and {123}, all with the same $\langle 111 \rangle$ Burgers vector, in agreement with the generally observed slip modes in bcc metals.

Table 5.2 Slip systems in the hexagonal α phase [4, 5]

Slip system	Burgers vector	Slip directions	Slip planes	No. of slip systems	
				Total	Independent
1	$\vec{a}$	$\langle 11\bar{2}0 \rangle$	(0002)	3	2
2	$\vec{a}$	$\langle 11\bar{2}0 \rangle$	$\{10\bar{1}0\}$	3	2
$\bar{2}_3$	$\vec{a}$	$\langle 11\bar{2}0 \rangle$	$\{10\bar{1}1\}$	6	4
4	$\bar{c}+\bar{a}$	$\langle 11\bar{2}3 \rangle$	$\{10\bar{2}2\}$	6	5

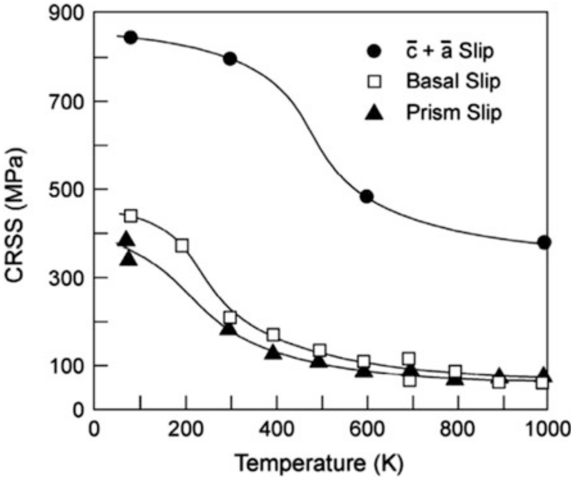


Fig. 5.2 Temperature dependence of CRSS for slip with $\vec{a}$ and $\vec{c}+\vec{a}$ Burgers vectors in single crystals of Ti–6.6Al [6]

5.2.5 *Alloying Additions*

Alloying elements in titanium are usually classified into α- or β-stabilizing additions, depending on whether they increase or decrease the α/β transformation temperature of 882 °C of pure titanium. The substitutional element Al and the interstitial elements O, N and C are all strong α-stabilizers and increase the transformation temperature with increasing solute content, as can be seen from the schematic phase diagram in Fig. 5.3a.

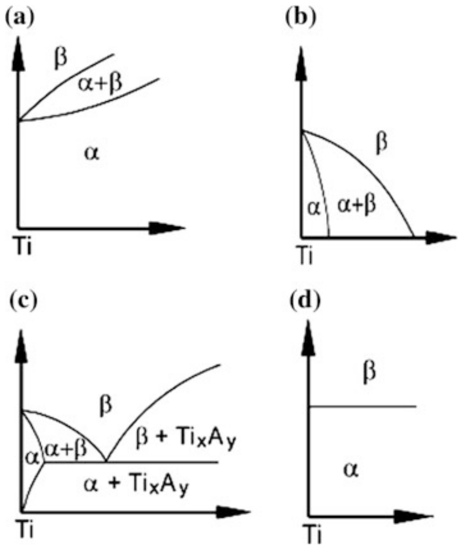


Fig. 5.3 Schematics showing the effects of alloying elements on titanium alloy phase diagrams: **a** α stabilizers, **b** isomorphous β stabilizers, **c** eutectoid β stabilizers (A = Fe, Cr or Si) and **d** neutral

Aluminium is the most widely used alloying element in titanium alloys, because it is the only common metal that raises the transition temperature and has extensive solubility in both the α and β phases. Among the interstitial elements, oxygen can be considered as an alloying element when the oxygen content is used to obtain the desired strength level, as in different grades of CP titanium. Other α stabilizers include B, Ga, Ge and the rare earth elements, but their solid solubilities are much lower as compared to aluminium or oxygen and none of these elements is commonly used as an alloying element.

The β-stabilizing elements are divided into β-isomorphous elements and β-eutectoid-forming elements, depending on the details of the binary phase diagrams. These are shown schematically in Fig. 5.3b, c. The most frequently used β-isomorphous elements in titanium alloys are V, Mo and Nb. Sufficient concentrations of these elements make it possible to stabilize the β phase to room temperature by suppressing the martensitic reaction that can occur during the quenching of alloys with lower β stabilizer concentrations. Other elements belonging to this group that are rarely used, or not used at all because of density and melting point considerations, are Ta and Re.

Of the β-eutectoid-forming elements, Cr, Fe and Si are used in many titanium alloys (they can form compounds like Ti_xA_y as shown in Fig. 5.3c, where A is Cr, Fe or Si), whereas Ni, Cu, Mn, W, Pd and Bi have only very limited usage. Some of these latter elements are used only in one or two special purpose alloys. Other β-eutectoid-forming elements, such as Co, Ag, Au, Pt, Be, Pb and U, are not used in titanium alloys. **N.B**: It should be mentioned that hydrogen belongs to the β-eutectoid-forming elements. Hydrogen is undesirable in titanium alloys because it can cause embrittlement. Therefore the maximum hydrogen content in CP titanium and titanium alloys is strictly limited to about 125–150 ppm.

In addition, some elements (Zr, Hf and Sn) are considered neutral as shown in Fig. 5.3d, because they do not affect the α/β transformation (β transus) temperature, or lower it only slightly and then increase the transformation temperature again at higher concentrations. Zr and Hf are isomorphous with titanium and therefore they both undergo the same $\beta \rightarrow \alpha$ allotropic phase transformation. These elements have complete solubilities in the α and β phases of titanium. In contrast, Sn belongs to the β-eutectoid-forming elements, but has essentially no effect on the α/β transformation temperature.

Many commercial multi-component alloys contain Zr and Sn, but in these alloys both elements are considered as α-stabilizers. This is because of the chemical similarity of Zr to titanium and because Sn can replace or add to aluminium in the hexagonal-ordered Ti_3Al phase (α_2). When present with aluminium, Sn behaves as an α stabilizer. This example shows that the interactions between alloying elements make it difficult to understand titanium alloying behaviour on the basis of binary Ti-*X* systems. Rosenberg [8] attempted to express the effect of α-stabilizing elements in multi-component titanium alloys as an equivalent aluminium content by the following equation:

$$[\mathrm{Al}]_{\mathrm{eq}} = [\mathrm{Al}] + \frac{[\mathrm{Zr}]}{6} + \frac{[\mathrm{Sn}]}{3} + 10[\mathrm{O} + \mathrm{C} + \mathrm{N}] \tag{5.1}$$

Similarly, the potency of β-stabilizers is measured in terms of an equivalent molybdenum content by the following equation [9]:

$$\begin{aligned}[\mathrm{Mo}]_{\mathrm{eq.}} = {} & [\mathrm{Mo}] + 0.67[\mathrm{V}] + 0.44[\mathrm{W}] + 0.28[\mathrm{Nb}] + 0.22[\mathrm{Ta}] \\ & + 1.6[\mathrm{Cr}] + 1.25[\mathrm{Ni}] + 1.7[\mathrm{Co}] + 2.9[\mathrm{Fe}] - 1.0[\mathrm{Al}]\end{aligned} \tag{5.2}$$

where [*X*] indicates the wt% concentration of each element.

As already mentioned, aluminium is the most important α-stabilizer and is therefore present in most titanium alloys. The binary Ti–Al phase diagram, Fig. 5.4, shows that with increasing aluminium content the Ti_3Al (α_2) phase will be formed and that the two-phase region (α + Ti_3Al) starts at about 6.5 wt% Al for a temperature of about 500 °C (indicated by the black arrow). This value also decreases with increasing oxygen content. To avoid any appreciable amount of Ti_3Al precipitates in the α phase, the aluminium content in most titanium alloys is limited to about 6 wt%. From Fig. 5.4 it can be seen that for 6 wt% aluminium the α/β transformation temperature is increased from 882 °C (0 % Al) to about 1000 °C for the narrow two-phase (α + β) region.

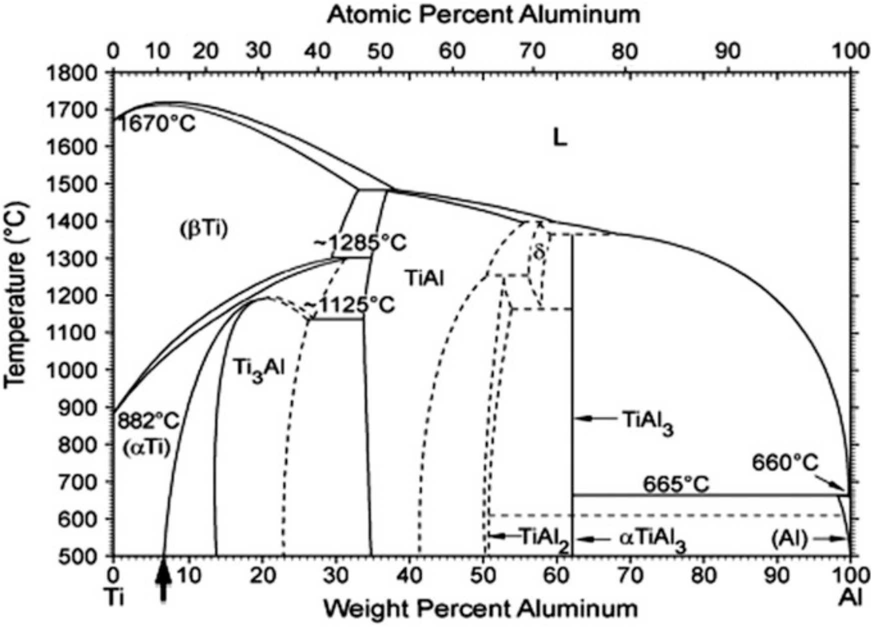


Fig. 5.4 Ti–Al phase diagram [10]: the *black arrow* points to an aluminium composition of 6 wt% Al, which is about the limit for aluminium additions to most titanium alloys

In addition to conventional titanium alloys, the Ti–Al phase diagram is also the basis for the so-called titanium aluminides, which are recently developed alloys based on the two intermetallic compounds based on Ti_3Al (Alpha-2 alloys), and a ternary orthorhombic variant based on Ti_2AlNb and TiAl (Gamma alloys).

5.2.6 Phase Transformations

Titanium alloy systems include several types of phase transformations. Transformation of the bcc β phase to the hexagonal α phase in CP titanium and titanium alloys can occur martensitically, as mentioned earlier, or by a diffusion-controlled nucleation and growth process, depending on cooling rate and alloy composition. The crystallographic orientation relationship between α and β was first studied (*for zirconium*) by Burgers [11] and is therefore named the Burgers Orientation Relationship (BOR):

$$(110)_\beta \| (0002)_\alpha$$
$$[111]_\beta \| [11\bar{2}0]_\alpha$$

The closest-packed bcc (110) plane maps onto the close-packed hcp (0002) plane, and the close-packed directions are congruent. This relationship was also confirmed for titanium [12].

According to the BOR, a bcc crystal can transform to 12 hexagonal variants that have different orientations with regard to the parent β crystal. The BOR is closely obeyed for both the conventional nucleation and growth process and for the martensitic transformation.

Martensitic transformation The martensite transformation in titanium alloys involves the cooperative movement of atoms by a shear-type process, resulting in a microscopically homogeneous transformation of the bcc crystal lattice into the hcp lattice over a given volume. The hexagonal martensite is designated α' and is observed in two morphologies: massive martensite (lath or packet martensite) and "acicular" martensite [13].

With increasing solute content the hexagonal structure of the martensite becomes distorted, losing its hexagonal symmetry and then is properly described as orthorhombic [13]. This orthorhombic martensite is designated α''. This martensite can also be stress-induced, as may occur in certain alloys like Ti–10V–2Fe–3Al that are at the borderline of stability/metastability.

Titanium martensites are not as hard as steel martensites and cause only marginal strengthening, since there is no appreciable distortion of the lattice by the substitutional solutes such as Al or V.

Athermal and isothermal ω phase formation Although not relevant to any practical application of titanium alloys, it should be mentioned that in many alloys in which the martensitic reaction is suppressed, the β phase decomposes athermally upon quenching to form the metastable athermal ω phase. This has been suggested to be a precursor to the martensitic reaction because the athermal transformation involves a shear displacement in the ⟨111⟩ direction of the bcc lattice [14], although this has not been proven. However, the ω particles may serve as nucleation sites for α phase precipitation.

The ω phase can also form isothermally during low temperature ageing of β alloys. However, ω phase formation is generally detrimental to the mechanical properties, and is usually avoided.

Nucleation and diffusion-controlled growth transformation When titanium alloys are cooled at sufficiently low rates from the β phase field into the (α + β) phase field, the α phase, which is incoherent with respect to the β phase, first nucleates preferentially at β grain boundaries, leading to a more or less continuous α layer along β grain boundaries. During continued cooling, α plates nucleate either at the interface of the continuous α layer or at the β grain boundary itself and grow into the β grain as parallel plates (so-called α colonies) [15]. They continue to grow into the β grain interior until they meet other α colonies nucleated at other grain boundary areas of the β grain. An example of such a microstructure is shown in Fig. 5.5a.

With increasing cooling rate the size of the α colonies as well as the thicknesses of the individual α plates become smaller. Colonies nucleated at β grain boundaries cannot fill the whole grain interior anymore, and colonies also start to nucleate on

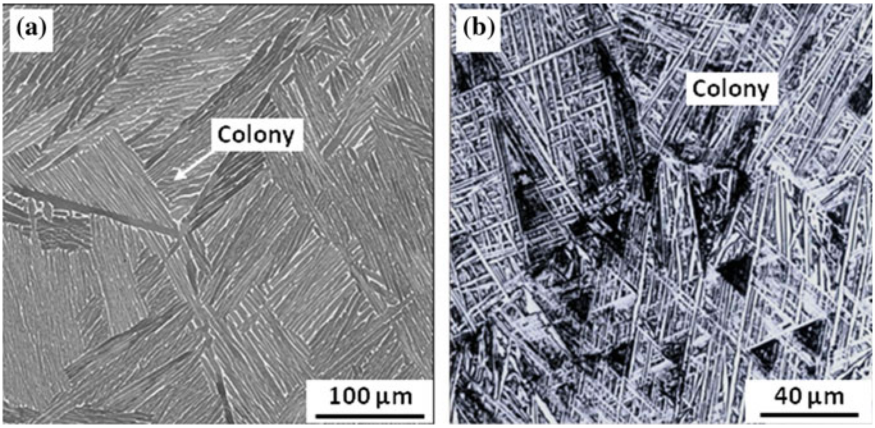


Fig. 5.5 Microstructures in alloy Ti–6Al–4V after cooling from the β phase field: **a** slow cooling resulting in a colony-type structure and α phase at prior β grain boundaries, and **b** faster cooling resulting in a basketweave/Widmanstätten structure

the boundaries of other colonies. To minimize the overall elastic strains the new α plates nucleating by "point" contact on the broad face of an existing α plate tend to grow nearly perpendicular to that plate. This selective nucleation and growth mechanism in combination with the smaller plates within the colonies leads to a characteristic "basketweave" or Widmanstätten microstructure, as shown in Fig. 5.5b.

5.3 Primary Processing: Melting and Consolidation

This section describes the procedures used to formulate titanium alloys and the melting technology used to produce ingots, which are the starting materials for both mill products and remelt stock for titanium castings. The solidification of the molten metal is the key to obtaining homogeneous, high-quality ingots for conversion to mill products. Melt-related defects must be minimized for titanium to perform at a level that justifies its cost and meets the intent of its use, especially in critical components like discs in aeroengines. This means that sophisticated and capital-intensive methods are used to melt titanium and produce sound, homogeneous ingots.

Molten titanium is very reactive, and special means are required to produce ingots of unalloyed titanium and titanium alloys. Titanium and its alloys are melted either in a vacuum arc remelting (VAR) furnace or in a cold hearth melting (CHM) furnace. In both cases melting is done in a manner that prevents molten titanium from contacting furnace refractories such as those used in vacuum induction melting (VIM) furnaces.

5.3.1 Vacuum Arc Remelting (VAR)

First melt electrode This consists of mechanically compacted blocks of titanium sponge and alloying elements that are welded together in an inert gas chamber. Each block has the desired nominal alloy composition from being mixed in a twin cone blender. Because titanium is expensive, there is a strong incentive to recycle and reuse titanium scrap (often called revert), including turnings and chips from machining. This reuse is accomplished for both unalloyed grades and alloys by welding appropriate-grade scrap to the electrode.

Scrap control and usage Revert is carefully controlled with regard to its origin and cleanliness. For example, scrap that has been flame-cut is generally not allowed. Experience has shown that the nitrogen- and carbon-enriched regions along the flame-cut edges are not always refined out during melting. This can leave interstitial-stabilized defects in the final product. Also, machine turnings from component manufacture are subject to special controls. The turnings must be cleaned to remove any residual cutting fluids and X-rayed to ensure that they contain no WC cutting tool fragments or other high-density inclusions (HDIs) that can end up in the ingot.

Master alloys Most of the β-stabilizing elements with higher densities and melting points, like Nb, Mo and V, are preferably added in the form of aluminium-based master alloys (Al–V, Al–Mo, Al–Nb, etc., in different ratios). These master alloys reduce the chance of alloy segregation.

VAR production of homogeneous, sound ingots of titanium alloys requires care and detailed attention to the melting procedure, which varies for particular alloys. Over the past several decades, dozens of improvements have been made to the process, some major and some minor. All have been directed towards reducing the possibility of defects and the extent of variation in the ingots. Figure 5.6 shows a schematic of the VAR process.

The VAR-melted ingots can be melted two or three times, depending on the intended end use of the material. There are a number of parameters that must be monitored and controlled to ensure homogeneity and soundness of the ingots:

- The furnace vacuum is continuously monitored to ensure that no air or small water leaks contaminate the melt with nitrogen or oxygen (major water leaks create an explosion hazard).
- The melt rate is continuously adjusted to control the size of the molten pool at the top of the ingot. In segregation-prone alloys, such as Ti– 17 or Ti–10V–2Fe–3Al, it is common to melt smaller ingots, less than 75 cm in diameter, and melt at lower rates (5–6 kg/min instead of 8–10 kg/min). This modified melt practice

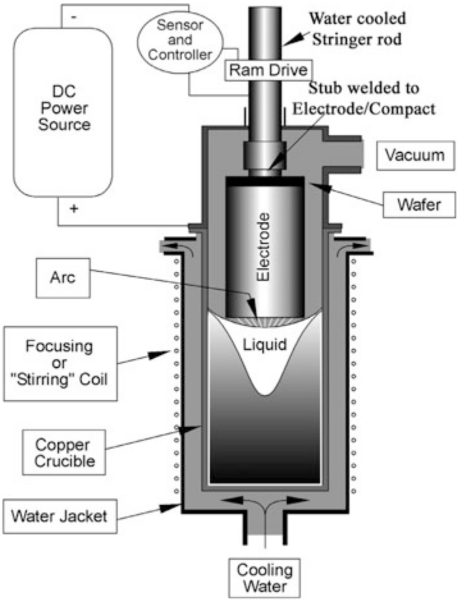


Fig. 5.6 Schematic of VAR furnace and ingot during a second melt: the electrode being remelted is at the *top*, and the new ingot is at the *bottom*

creates a smaller, shallower molten pool at the top of the ingot. The lower melt rates use correspondingly lower power settings (200–275 kVA instead of 400–500 kVA).

- At the top of the ingot mould most VAR furnaces have electrical coils to create an electromagnetic field to stir the molten metal and improve the ingot homogeneity.
- As the final part (25–35 %) of the ingot is approached, the melt rate is reduced by reducing the power in several steps. This procedure minimizes the extent of shrinkage pipe formation and other melt-related defects such as type II at the ingot top. (See Sect. 5.3.3 for discussion of melt-related type I and type II defects.)

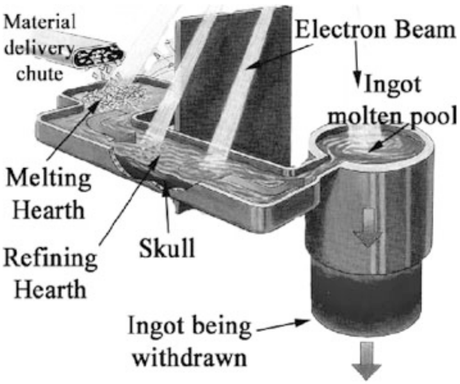
5.3.2 *Cold Hearth Melting (CHM)*

Cold hearth melting (CHM) is a relatively new melting method (see Fig. 5.7) that has several advantages over the VAR process and is now widely used for aero-engine disc grade alloys. This method uses a water-cooled copper vessel (the hearth), which contains the molten alloy. Melting is done using either a plasma arc or an electron beam as the heat source. In both cases the heat input is balanced against the rate of heat extraction from the water-cooled copper hearth. This maintains a thin layer of solid titanium alloy (called the “skull”) in contact with the hearth, so the molten titanium alloy only contacts the solid titanium alloy. This prevents any contamination by the hearth.

The potential advantages of CHM include the following:

- It permits the residence time of the titanium alloy in the molten state to be controlled independently of the volume of molten metal solidifying as an ingot. This enables refining by dissolution of any nitrogen- or oxygen-rich defects

Fig. 5.7 Schematic of a CHM furnace [1]



without incurring a large, deep molten metal pool (as in the VAR process) that can cause solute segregation.

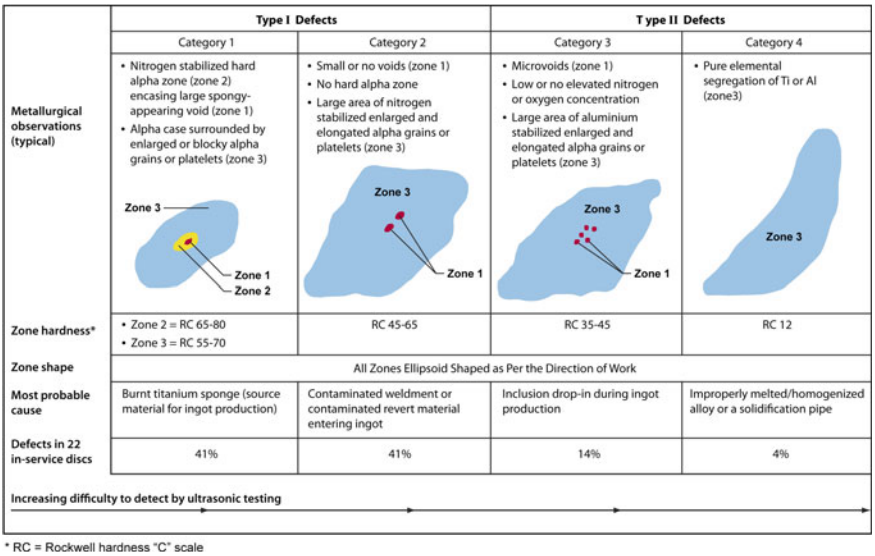
- It automatically introduces gravity separation of HDIs such as WC tool fragments or tungsten welding electrode tips that may be introduced along with the revert. This contrasts with the VAR process, where all of the material in the electrode ends up in the ingot.
- It allows direct casting of non-axis symmetric shapes, such as slabs or bars. These cast products are much better suited for conversion to flat mill products (plate, sheet and strip) than large round ingots. Consequently, the conversion losses are lower and products made this way can be more cost competitive. This capability has proved to be particularly attractive for making sheet and strip from alloys that are readily rolled into coils without reheating.
- In contrast to the physical environment in the VAR furnace chamber, the CHM furnace is more conducive to the use of online sensors, and hence is more amenable to real-time process controls and detection of process variations during melting.

5.3.3 Melt-Related Defects

Experience has shown that, once formed, melt-related defects are very difficult to eliminate and can have an extremely detrimental impact on material performance. Melt-related defects can be categorized as either intrinsic or extrinsic, depending on their origin. Extrinsic defects are caused by inadvertent introduction of impurities during preparation of the electrode or during the melt process. Intrinsic defects are those that can be present if ingot solidification occurs without proper control. The nature and origin of melt-related defects in VAR material are discussed in Ref. [16], and Fig. 5.8 shows a schematic of the types of defects.

Type I defects The reactivity of titanium creates the possibility of formation of interstitial-stabilized inclusions. These are known as Type I defects and are most frequently the nitrogen-rich compound TiN. The nitrogen-stabilized Type I inclusions are very hard and brittle and often called “hard alpha”. Consequently, they fracture at relatively low stresses leading to incipient cracks in the material. Type I inclusions also can have high concentrations of oxygen and/or carbon, but this is less common.

Because of the propensity to crack at low strains, a Type I inclusion can seriously decrease the fatigue capability of the material. Over the past 25 years, numerous restrictions have been placed on both input material and on melt practice with the goal of minimizing the presence of type I inclusions in titanium alloy products. Today, the frequency of Type I defects detected in aeroengine disc grade titanium alloys is less than one defect per every 500,000 kg of material melted.



	Type I Defects		Type II Defects	
	Category 1	Category 2	Category 3	Category 4
Metallurgical observations (typical)	• Nitrogen stabilized hard alpha zone (zone 2) encasing large spongy-appearing void (zone 1) • Alpha case surrounded by enlarged or blocky alpha grains or platelets (zone 3)	• Small or no voids (zone 1) • No hard alpha zone • Large area of nitrogen stabilized enlarged and elongated alpha grains or platelets (zone 3)	• Microvoids (zone 1) • Low or no elevated nitrogen or oxygen concentration • Large area of aluminium stabilized enlarged and elongated alpha grains or platelets (zone 3)	• Pure elemental segregation of Ti or Al (zone3)
Zone hardness*	• Zone 2 = RC 65-80 • Zone 3 = RC 55-70	RC 45-65	RC 35-45	RC 12
Zone shape	All Zones Ellipsoid Shaped as Per the Direction of Work			
Most probable cause	Burnt titanium sponge (source material for ingot production)	Contaminated weldment or contaminated revert material entering ingot	Inclusion drop-in during ingot production	Improperly melted/homogenized alloy or a solidification pipe
Defects in 22 in-service discs	41%	41%	14%	4%

Increasing difficulty to detect by ultrasonic testing

* RC = Rockwell hardness "C" scale

Fig. 5.8 Survey of possible VAR melt-related defects in titanium alloys [17]

However, since the aeroengine industry uses over 1,000,000 kg of titanium alloys each year, the detection and elimination of defects are still essential.

The most effective inspection method is ultrasonic inspection. The basis for detection is the void that usually accompanies the defect. A void occurs owing to the strain incompatibility between the matrix and the hard TiN inclusion. In principle the TiN should be detectable, because it has a modulus about 30 % higher than the average value of the titanium alloy matrix. In practice this modulus difference is about the same as the elastic anisotropy of α titanium. Thus any ultrasonic technique sensitive enough to detect such differences will also detect regions of texture or preferred orientation and lead to many false calls during ultrasonic inspection.

Type II defects These are Al-rich and usually the result of incorporation of Al-rich regions from the shrinkage pipe near the top of the ingot into the product. Type II defects are less detrimental to the alloy properties than Type I defects; but in high strength alloys such as Ti-17 these defects do not respond to heat treatment (ageing) in the same way as the surrounding matrix, and therefore remain softer. Consequently, they will deform preferentially in fatigue situations, leading to earlier crack nucleation. Type II defects are eliminated by proper melt practice and cropping the part of the ingot top that contains the shrinkage pipe. It is also possible to minimize them by ingot homogenization (see below).

Beta flecks These are due to alloy segregation. Alloys that contain β-eutectoid forming elements, in particular Fe and Cr, typically have depressed freezing temperatures, resulting in solidification over a significant temperature range. This situation can lead to Fe or Cr segregation during ingot solidification. Alloys that contain only β-isomorphous alloying additions, such as Mo, V and Nb, do not have similarly depressed solidification temperatures, and these alloys are much less prone to freezing segregation.

Segregation of Fe or Cr during freezing results in regions that have a lower β transus temperature. These regions have a different microstructure compared to the surrounding material in the final product. These solute-rich regions sometimes become clearly visible in materials heat-treated below but near the nominal β transus, and are known generally as “beta flecks”. Figure 5.9 shows examples of beta flecks: note the large prior β grains and the lower volume fraction of α (the light-etching phase) in Fig. 5.9c. The segregated areas typically occur on a scale ranging from a few hundred micrometres to a few millimetres. These solidification-related defects *can* occur in any titanium alloy, but as mentioned earlier, alloys containing eutectoid-forming elements, such as Cr or Fe, are considerably more susceptible.

Like Type I and type II defects, beta flecks are detrimental to the fatigue strength. However, beta flecks more resemble Type II defects in their fatigue behaviour, since they are weaker than the matrix and deform preferentially, leading to early crack nucleation. Also, like Type II defects, beta flecks can be minimized by proper melt practice and by ingot homogenization.

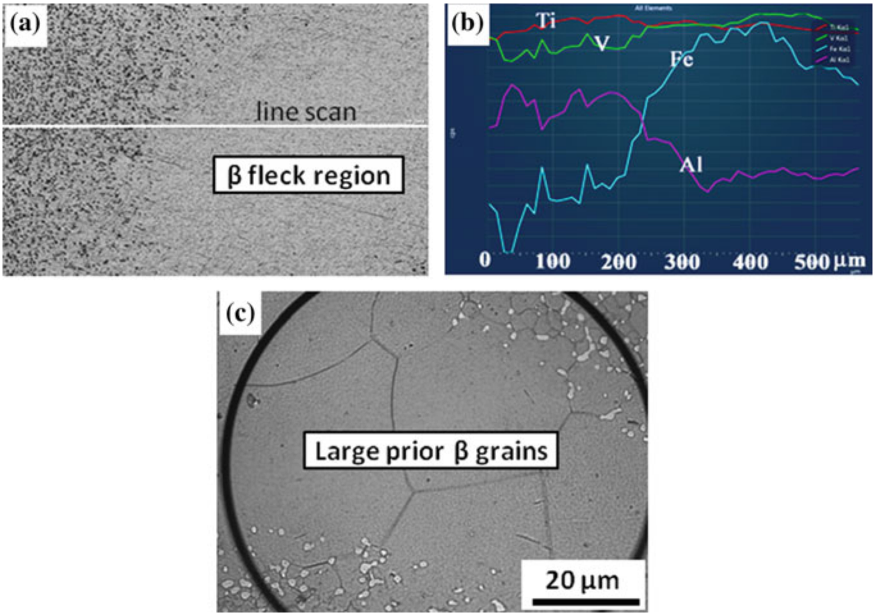


Fig. 5.9 Beta flecks in the alloy Ti–10V–2Fe–3Al **a** showing an SEM image of a beta fleck region; **b** EDAX line scanning of the image in (**a**); and **c** optical image of an etched beta fleck region

5.3.4 Conditioning and Homogenization

Irrespective of melt practice, after completion of the final melt process and before hot working the ingot undergoes conditioning. Conditioning creates a smoother ingot surface free from stress concentrations that could induce cracking during the ingot breakdown and conversion operations. This conditioning can be done by grinding or lathe turning of cylindrical ingots, or by grinding of slabs. Grinding is often done manually and care must be taken to control the surface temperature increase during grinding. If not done carefully, the temperature can get high enough to create interstitial-stabilized regions that can subsequently be retained in the final product.

Once the ingot is conditioned it is generally given a homogenization anneal in the β phase field prior to working. Not all titanium producers use a homogenization treatment, and not all producers do this for all alloys. When a homogenization treatment is used, the times and temperatures are alloy-dependent, but are typically 200–450 °C above the β transus for times of 20–30 h. It is important to emphasize that homogenization does not remove HDIs such as WC and Type I (hard alpha) defects.

5.4 Secondary Processing

5.4.1 Forging

Initial working (also called ingot breakdown) This is done on a forging press at a temperature of about 150 °C above the β transus. During this operation the initial round ingot is converted into a square or round-cornered square workpiece. The amount of initial strain before the first necessary reheat is typically 28–38 %, although it is somewhat alloy-dependent and also depends on whether the ingot has been homogenized.

The workpiece is fan-cooled after the initial working operation, and then is reheated to 35–50 °C below the β transus, i.e. within the (α + β) phase field. It is then given a further reduction of about 30–40 % to recrystallize it and refine the structure in preparation for continued hot working. After this reduction the workpiece is air-cooled. The workpiece is then reheated to about 50 °C above the β transus and worked another 30–40 %, followed by a rapid cool (Ti–6Al–4V is water quenched, other alloys such as Ti-17 or Ti-10-2-3 are aggressively fan-cooled).

The basic intent of this initial heating, working, cooling, reheating, working and cooling is to improve the compositional homogeneity and thus the structural uniformity of the alloy workpiece. This improves its subsequent response to thermomechanical processing operations. The remaining hot working operations are typically done in the (α + β) phase field. A minimum of 65 % additional reduction is typically used to obtain uniform structures that will respond to forging or heat treatment and are more amenable to ultrasonic inspection.

N.B: In segregation-prone alloys, where the initial ingot size is smaller, an upsetting operation may be used to provide a large enough diameter workpiece that will yield a large diameter billet to enable maintaining the reductions mentioned above.

Secondary working steps These are mainly determined by the shape of the product form that the ingot is destined to become (billet, plate, sheet or bar). Before continuing, the workpiece is inspected for surface cracks or tears and any sharp discontinuities that could propagate during continued working. If present, these are blended out during a conditioning operation.

There are basically four types of titanium alloy mill products: billet, bar, flat-rolled product (plate and sheet) and casting electrode:

- Billet is typically round and is used as the input material for forgings and rolled rings.
- Bar can be round, square or shaped during rolling to meet a special need.
- Plate is a flat-rolled product thicker than about 25 mm.
- Sheet is a flat-rolled product up to a thickness of about 25 mm.
- Casting electrode is remelted by the casting producer and hence must have a billet-like shape, but it is shaped to the desired diameter and cut to length without regard for the need to create a particular microstructure, since it will be remelted.

Billet and Bar Billet and large diameter bar are made using a rotary general forging machine (GFM) or a forging press. Since billet is a semi-finished product used for making die forgings, the billet surface finish must be adequate to permit high sensitivity ultrasonic inspection. Depending on the alloy and the billet forging temperature, rough grinding or machining may be required.

Bar, on the other hand, is a finished product. Thus it always requires grinding or turning to impart an acceptable surface finish and uniform dimensions and shapes. A GFM gives a better surface finish and concentricity than a forging press, making the GFM product more economical. The other benefits from using GFMs are that they introduce uniform work into the product; they require fewer, if any reheats; and they are easy to control. Smaller diameter bar is finished in a rod mill that has a series of shaped rolls with successively smaller openings.

For both billet and bar the working temperature is normally in the ($\alpha + \beta$) phase field, typically 50–70 °C below the β transus. (Although there are exceptions when special properties are required from $\alpha + \beta$ alloys worked in the β phase field.)

N.B. Some important considerations:

1. Hot working requires close control. Titanium alloys have relatively poor thermal conductivity and relatively high flow stresses at all ($\alpha + \beta$) working temperatures. At high rates of deformation the thermal conductivity is too low to allow

heat dissipation, resulting in adiabatic heating. This can lead to localized flow softening in active shear bands, resulting in further strain localization and formation of intense shear bands. These result in non-uniform microstructures after recrystallization of the final product.

2. Under extreme circumstances the critical strain for ductile fracture is locally exceeded in the shear bands and small voids are formed. These voids are known as strain-induced porosity (SIP). (This SIP can also be created in plate, particularly if the working temperature is allowed to drop.)

   Once SIP is created in forging billet, it is not always healed during subsequent forging operations. Consequently, it can be carried over into a finished component as a fatigue-nucleating defect. SIP is typically small and can be difficult to detect by ultrasonic inspection.
3. Alternatively, adiabatic heating can be beneficial if it is properly managed, since it can extend the working time and deformation extent between reheats.

   An additional reason for careful control is that in alloys prone to beta fleck formation the adiabatic heating must not result in exceeding the local β transus in solute-rich regions of the workpiece, thereby perpetuating the microstructural inhomogeneity.

5.4.2 Rolling

Plate and sheet comprise 40 % of titanium mill products. Plate, sheet and small diameter bar (including rod) are all made in rolling mills with either flat or shaped rolls. Normally, a “four-high” rolling mill (each work roll is backed by a second roll) is used for hot rolling titanium alloy plate and sheet.

The starting material for plate and sheet is a forged bloom that is an intermediate product of the ingot conversion process. The bloom is hot-rolled into a slab, which then receives further hot reductions. The hot rolling operations may be done in either the β or the (α + β) phase fields, depending on the alloy and on the end properties desired. For plate the final hot reduction stops at the desired thickness. The plate is then given an annealing treatment before it is surface conditioned by grinding and/or pickling.

Flat-rolled products require reheating more frequently because the plane strain imposed during rolling increases the incidence of edge cracking. The final annealing treatment is typically more of a stress relief than a true anneal. For example, Ti–6Al–4V is often shipped to users in the so-called mill-annealed condition.

Mill annealing means that the plate has been held at about 700 °C for times as short as 1 h or as long as 8 h. N.B: At higher annealing temperatures the yield stress can be lower than the initial residual stresses. This can cause relaxation of internal residual stresses by gross plastic deformation of the plate, causing it to lose flatness during the annealing treatment. Holding for longer times will result in flatness recovery owing to creep flattening. Thus the flatness of the product after annealing is a function of the amount of work and the annealing time and temperature. Such plates are most frequently used for machining into aircraft parts.

Titanium alloy sheet is typically pack-rolled to avoid surface oxidation. In pack rolling, a group of sheet blanks are sealed in a steel retort and rolled as a group. The individual blanks have an inert “parting agent” between them to prevent bonding to one another during rolling. After hot rolling is completed the pack is cut open and the finished sheets are extracted, pickled and creep flattened or annealed in fixtures, depending upon the required flatness. Some final cold reduction also can be done to meet gauge and flatness requirements.

Sheet packs are often cross-rolled to widen the sheet. Cross-rolling also reduces the texture intensity (preferred crystallographic orientation) and the texture symmetry in the final product. Texture can be very important for the forming response of $\alpha + \beta$ alloy sheet, which tends to develop strong textures during hot working. This makes some properties (e.g. yield stress and modulus of elasticity) anisotropic, and this anisotropy must be taken into account during the design of structures and components made from sheet.

Strip is a sheet-like product, but typically narrower than sheet and very long. Strip is essentially unidirectionally rolled and coiled after the final rolling operation. The majority of strip is produced from one of the grades of CP titanium (usually Grade 2) or the alloy Ti–3Al–2.5V, both of which can be cold-rolled. The production of strip has enabled the economical production of welded CP titanium and Ti–3Al–2.5V tubing for aircraft heating and de-icing ducts. Beta 21S is a β titanium alloy which is also produced in strip form.

The early stages of strip production are identical to those for sheet and plate. However, at the slab stage the strip is hot-rolled, annealed, pickled, surface conditioned by grinding and coiled as hot band, which is the intermediate product used for cold rolling. It is then cold-rolled to gauge in a multi-stand mill such as a Steckel or Sendzimir mill. These mills use several rolls to back a pair of very small diameter work rolls, thereby ensuring the flatness of the thin, cold-rolled product. After cold rolling, the strip is annealed again and coiled for shipment. Because of the unidirectional working, strip always has a significant degree of texture, but because most strip is CP titanium, this is generally not a limitation.

5.5 Titanium Alloy Castings

The use of cast titanium components has grown over the past 10 to 15 years, owing to decreased costs and improvements in the casting process [18, 19]. The growth in the use of castings has resulted in fewer fabrication steps, by eliminating assembly from a number of parts. In some cases castings have replaced parts that were previously machined from forgings or heavy plate or billet. The substitution of castings for components made by other methods has been enabled by three factors:

- Improved net shape casting technology.
- Improved fatigue properties owing to the use of hot isostatic pressing (HIP) to heal internal porosity that can act as crack initiation sites.
- Decreased metal–mould reaction.

Casting of titanium alloys on a production scale is done using one of two methods: (i) conventional casting using rammed graphite moulds, and (ii) investment casting in ceramic shell moulds. Investment casting is more costly, but its shape-making capability makes the resulting castings economically attractive because they can displace very expensive forged and machined or fabricated parts.

Furthermore, as Fig. 5.10 illustrates, the investment casting method is capable of producing highly intricate shapes with essentially a net shape. In this case, this single-piece casting replaced welded and mechanically fastened frames that contained more than 100 individual parts including the fasteners.

After casting, the following steps are taken:

- Hot isostatic pressing (HIP-ing) to close any internal voids.
- Chemical milling to remove any reaction zone resulting from contact between the mould and the molten titanium alloy.
- Weld repair, if necessary, to close surface-connected defects due to shrinkage, hot tearing or incomplete mould-filling.
- Stress relief heat treatment (if necessary).
- Final simple chemical milling.

Weld repair of high-value castings allows these parts to be used instead of being scrapped, but the weld repair is labour-intensive and therefore costly. Weld repair is typically done using tungsten inert gas (TIG) welding. Depending on the sizes of the casting defects, metal in the form of weld filler wire may be used to repair them. It is expensive to make weld wire from all the high-performance alloys, including Ti–6Al–4V. However, for alloys available as sheet, narrow strips can be cut and used as filler.

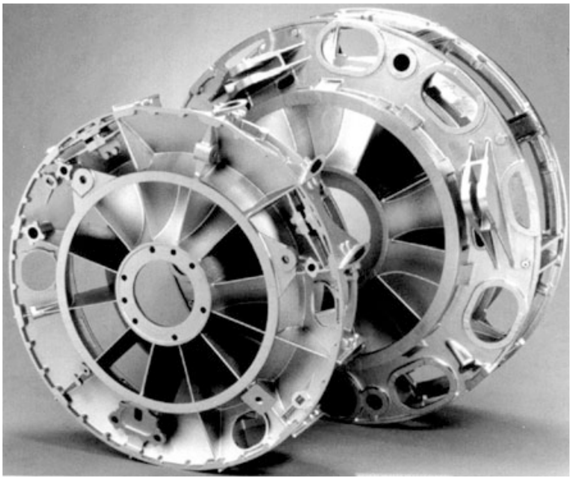


Fig. 5.10 Example of an investment cast aircraft engine frame [1]

Since weld repairs are costly, any improvements in casting technology would reduce the cost of titanium castings and could lead to an increased market share. An improved casting process currently under development is permanent mould casting. Permanent moulds have been used for casting lower melting point materials, e.g. Al and Mg and less reactive high melting point materials such as steel.

The challenge for permanent mould casting of titanium is to minimize the interaction of the molten metal with the mould while obtaining adequate superheating to permit good fill. Currently, castings of about 200 mm in maximum dimension represent the size limit that can be produced by titanium permanent mould casting. This limit is partly due to the sizes of available HIP pressure vessels.

5.6 Indian Scenario on Titanium Alloy Processing

The value of the titanium primary processing industry is well above US$ 1 billion. If secondary processing and manufacturing is added, the world figure is likely to be well in excess of US$ 2 billion.

In general, the issues for the titanium industry are mostly economical rather than technical, and have their origin in the too-close connection to the aerospace industry. This link has operated to the detriment of industrial developments that would otherwise give a wider market base and make titanium alloy production less dependent on aerospace demand cycles. The aerospace connection of titanium alloys has also resulted in production processes which are not suitable or too stringent for other industrial applications.

The present Indian scenario is very promising, specifically for aerospace grade titanium alloys. India is characterized by its vast reserves of rich ilmenite deposits all along its southern peninsular coasts. The reserves are estimated at 520 million tonnes (12–15 % of world total) and the reserves of rutile are estimated at 30 million tonnes in terms of TiO_2 content.

Mishra Dhatu Nigam Limited (MIDHANI), Hyderabad, is the only manufacturer in India having the capabilities for ingot melting and producing titanium mill products, starting from titanium sponge, which is imported at present. MIDHANI has been in operation since 1982 for the production of billets, plates, sheets, wire and seam-welded tubes for meeting indigenous demands. Also, the mineral separation unit of Kerala Minerals and Metals Ltd. (KMML), Sankaramangalam, has started producing aerospace quality titanium sponge for Indian applications: see Chap. 4 of this Volume of the Source Books.

The Indian Military Airworthiness regulatory body, i.e. the Centre for Military Airworthiness and Certification (CEMILAC), has approved MIDHANI for processing titanium alloys for aerospace and missile applications. There are many Indian programmes for indigenously produced and type-approved titanium alloys being produced at MIDHANI. Table 5.3 gives a detailed list of titanium alloys that are indigenously manufactured and provided with an airworthiness clearance.

Table 5.3 Type-approved and provisionally cleared indigenously produced titanium alloys

Alloy designation	Type	Form	Composition
BT 5-1	α Alloy	Forged and hot-rolled bars	Ti–5Al–2.5Sn
Titan 23A/OT4-1	Near-α alloy	Forged and hot-rolled bars	Ti–2Al–1.5Mn
		Cold-rolled sheets	
Titan 29A	Near-α alloy	Forged bars and HR bars	Ti–5.8Al–4Sn–3.5Zr–0.7Nb–0.5Mo–0.35Si–0.06C
Titan 26A (triple melted)	Near-α alloy	Forged bars	Ti–6Al–5Zr–0.5Mo–0.25Si
Titan 31A (triple melted)	$\alpha + \beta$ alloy	Forged and HR bars	Ti–6Al–4V
Titan 31A (double melted)		Forgings	Ti–6Al–4V
Titan 31 (Ti6Al4V ELI)		Forged and machined bars	Ti–6Al–4V (O < 1300 ppm)
BT 9-1	$\alpha + \beta$ alloy	Hot-rolled bars	Ti–6.5Al–3.3Mo–1.4Zr–0.25Si
BT 3-1	$\alpha + \beta$ alloy	Forged and HR bars	Ti–6.25Al–2Cr–2.5Mo–0.27Si–0.45Fe
Provisionally cleared alloys			
Titan 20A	CP Ti	Forged and HR Bars	Ti–0.4O
Titan 22A	α alloy	Hot-rolled/machined bars	Ti–8Al–1Mo–1V
Half alloy	$\alpha + \beta$ alloy	Forged and machined bars	Ti–3Al–2.5V
GTM 900	$\alpha + \beta$ alloy	Forged and hot-rolled bars and slabs	Ti–6.5Al–3.3Mo–1.4Zr–0.25Si
Titan 1023	Metastable β alloy	Forged and hot-rolled bars	Ti–10V–2Fe–3Al

5.7 Summary

In this chapter the basic crystallography and deformation modes of titanium alloys have been briefly considered. The different alloying elements of titanium and their use have been mentioned, and the melting techniques for industrial scale melting of titanium alloys have been described. The VAR process is generally more prevalent, but CHM is gaining popularity. In India VAR is the main industrial melting process, while the CHM electron beam melting process is becoming established. Common types of melt-related defects have also been discussed. Finally, ingot processing and casting techniques have been broadly described for wrought and cast products.

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