3 Technological Aspects

This chapter addresses the various aspects that are associated with producing titanium as a commercial material (hence “Technological Aspects”). It commences with a short discussion of the production of metallic titanium (titanium sponge), then continues with a discussion of all aspects of titanium production ranging from melting, including alloying (Sect. 3.2), to processing into useful product forms (Sect. 3.3). Included are products, such as billet, bar, plate, and sheet. Section 3.4 describes shaping processes for the manufacture of components. The emphasis in Sect. 3.5 is on near net shape processes, since these are one means of reducing the cost of using titanium alloys, which is a principal constraint to their increased use. Section 3.6 addresses the joining methods most commonly used for titanium and its alloys, and in Sect. 3.7 various surface treatment processes are described. Section 3.8 illustrates some of the inspection methods used during production of titanium mill products and components. Especially those used for high performance applications are described. Finally, it concludes in Sect. 3.9 with a discussion of characterization methods, which are particular to titanium alloys.

3.1
Sponge Production

Metallic titanium, as obtained from the ore, is called sponge. This is because it is porous and has a sponge-like appearance. Titanium as a chemical species is very abundant. It is the fourth most prevalent metallic element in the earth’s crust (only exceeded by Al, Fe, and Mg). The starting ore for the production of titanium is either rutile (TiO_2) or ilmenite ($FeTiO_3$). The extraction of metallic titanium from these ores occurs in five distinct stages or operations:

- Chlorination of the ore to produce $TiCl_4$.
- Distillation of the $TiCl_4$ to purify it.
- Reduction of the $TiCl_4$ to produce metallic titanium (the Kroll process).
- Purification of the metallic titanium (the sponge) to remove by-products of the reduction process.
- Crushing and sizing of the metallic titanium to create a suitable product for subsequent melting of CP titanium and titanium alloys.

The chlorination process starts with relatively impure rutile. If the ore is ilmenite instead of rutile, the starting material is TiO_2 enriched slag that is a by-product of the electromelting of ilmenite with carbon to produce iron. Chlorination occurs in a fluidized bed containing TiO_2, carbon (coke), and impurities that accompany the rutile into the chlorinator as shown schematically in Fig. 3.1. As shown, Cl_2

(gaseous) is introduced at the bottom of the chlorinator and contacts the (impure) TiO_2 and carbon reactants. The reaction products are metal chlorides (MCl_x), CO_2, CO, and gaseous $TiCl_4$ (the boiling point of $TiCl_4$ is 136ºC). These products are removed at the top of the reactor vessel and go directly into the fractional distillation unit (Fig. 3.2).

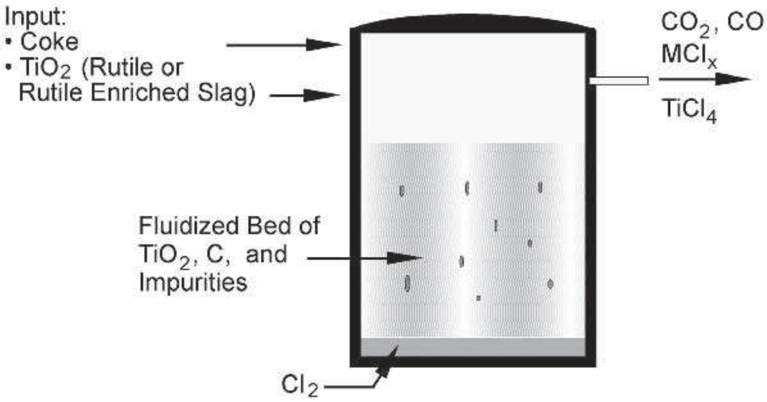


Fig. 3.1. Schematic drawing of a fluidized bed chlorinator used for producing $TiCl_4$ (courtesy J. A. Hall)

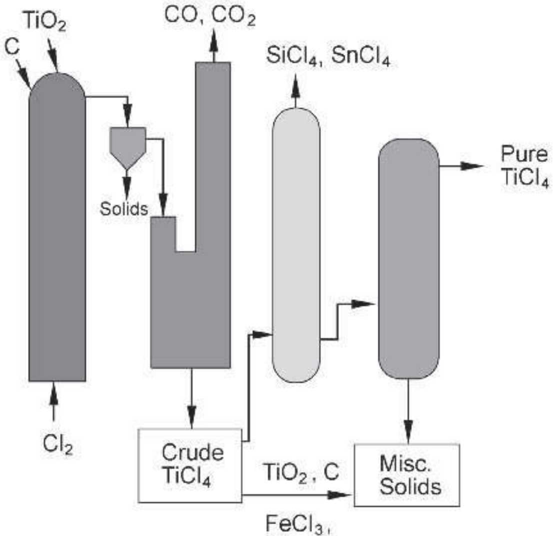


Fig. 3.2. Schematic drawing of a chlorinator on the left feeding the fractional distillation unit (two columns in the center) and a holding vessel on the right (courtesy J. A. Hall)

The basic chlorination reactions are as follows:

$$TiO_2 + 2Cl_2 + C \rightarrow TiCl_4 + CO_2$$

and

$$TiO_2 + 2Cl_2 + 2C \rightarrow TiCl_4 + 2CO.$$

The second step in the production route is the distillation process because the starting grade of $TiCl_4$ that comes from the chlorination process requires further purification. This is accomplished by fractional distillation of the $TiCl_4$ as shown in Fig. 3.2. Here it can be seen that a two step distillation process is used. The first step removes the low boiling point impurities such as CO and CO_2 and the second removes the higher boiling point impurities such as $SiCl_4$ and $SnCl_4$. The purified $TiCl_4$ is stored under inert cover gas until it is used.

The next stage in the production route is the reduction of the $TiCl_4$, the Kroll process. The purified $TiCl_4$ is put into a reactor filled with inert gas and already containing metallic Mg and heated to 800-850ºC to drive the following overall reduction reaction:

$$TiCl_4 + 2Mg \rightarrow Ti + 2MgCl_2.$$

This actually occurs in two steps as follows:

$$TiCl_4 + Mg \rightarrow TiCl_2 + MgCl_2$$

followed by

$$TiCl_2 + Mg \rightarrow Ti + MgCl_2.$$

A schematic of a Kroll reaction vessel is shown in Fig. 3.3 with the vessel on the left coupled to a vacuum distillation vessel on the right. The reduction reactions were originally studied by Kroll [3.1] in the late 1930's and the reduction of $TiCl_4$ by Mg is still known as the Kroll process. The metallic titanium, that is the product of the final reduction shown above, is in itself quite pure, but occurs as a mixture of pure metal and $MgCl_2$. Most of the $MgCl_2$ is removed continually as the Kroll reaction proceeds but there is some residual amount that must be removed during the metallic titanium extraction step described later.

Because the reduction reaction is exothermic, the $TiCl_4$ is added to the vessel containing Mg at a rate that allows the temperature to be managed. This is necessary to prevent the solid reaction product from becoming so dense that the volatile products are trapped inside. This reaction product is a solid mass of intermingled mixture of metallic titanium and $MgCl_2$. This is called a "sponge cake" and is the product of the Kroll process.

Earlier (1910), Hunter [3.2] had demonstrated that $TiCl_4$ could be reduced using molten Na and this method of making sponge is called the Hunter process. During the 1960-1995 period significant quantities of titanium sponge were produced using this process. Today, there are no large scale titanium production operations left that use this process. This is mainly because the economics of using Mg as the reducing agent are more attractive than using Na.

The next step in the production route is the extraction of the metallic titanium from the sponge cake by removal of the residual $MgCl_2$. Separation of the $MgCl_2$ can be done by one of several methods: acid leaching, inert gas sweep, or vacuum distillation. The former of these processes utilizes the preferential solubility of $MgCl_2$ in acidic solution, allowing removal of the $MgCl_2$ from the crushed sponge cake in a separate leaching operation. This process is no longer used extensively. The other processes have the advantage of removing the $MgCl_2$ in situ in the Kroll reactor vessel. These processes utilize the high vapor pressure of $MgCl_2$ to selectively remove it by evaporation and then recondense it for Mg and Cl_2 recovery away from the sponge. The inert gas method uses argon as a carrier gas to transport the $MgCl_2$ vapor.

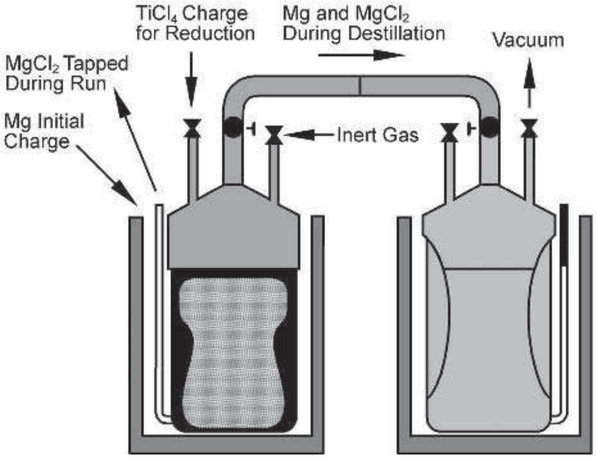


Fig. 3.3. Schematic of a Kroll reaction vessel on the left coupled with a collection vessel on the right for the Mg and $MgCl_2$ that are removed during the vacuum destillation (courtesy J. A. Hall)

The vacuum distillation process (VDP) is shown schematically in Fig. 3.3. In this process, the sponge cake is heated in situ in the Kroll reactor vessel on the left under vacuum. This allows the volatile $MgCl_2$ and excess metallic Mg to be extracted by evaporation and recondensed in another vessel (the one on the right in Fig. 3.3). This vessel becomes the Kroll reaction vessel for the next reduction run after additional Mg is added. The left hand vessel in Fig. 3.3 containing the metallic titanium sponge cake is then replaced by an empty one. This process is a semi-continuous one which is economically advantageous. The resulting vacuum distilled sponge has the lowest volatile content of the three sponge purifying processes. Because of the high temperature (700-850°C) at which VDP is conducted, the sponge does pick up small amounts of Fe and Ni from the stainless steel reaction vessel. The Ni is especially undesirable in high temperature alloys, since Ni reduces the creep strength when exceeding specific limits. There also is some sintering of the sponge cake.

In both processes (inert gas sweep and VDP), the Mg and Cl_2 are recovered and recycled. Today, Mg reduced titanium sponge production is nearly a closed loop batch process with only modest amounts of "make up" Mg and chlorine being required from batch to batch.

The last stage in the production route is the crushing and sizing of the titanium sponge. After removal of the excess Mg and $MgCl_2$, the sponge mass is crushed to produce granules of metallic titanium. After crushing and sizing, the coarser sponge granules are further sheared to reduce their size. These crushing and shearing operations are conducted in air but require care. Titanium is potentially pyrophoric and any fires that occur during this operation can contaminate the sponge with nitrogen rich regions that later result in melt related defects. Higher VDP temperatures reduce the ease of subdividing the sponge cake. Unless otherwise specified, titanium sponge producers typically do not strive for average sponge particle sizes less than 3-5 cm. This eliminates the cost of further crushing or shearing operations and avoids the threat of incurring sponge fires during these operations. The desired or specified sponge particle size depends on the end product that is being produced. Coarser granules (up to 2.5 cm) can be used for commercially pure titanium (CP titanium) and standard grades of most alloys, but for high performance applications, such as aircraft engine rotors, smaller sizes (1 cm maximum) are typically required. This is because of the concern for interstitial stabilized defects in the melted product for rotor grade material. Examples of these sponge particles are shown in Fig. 3.4.

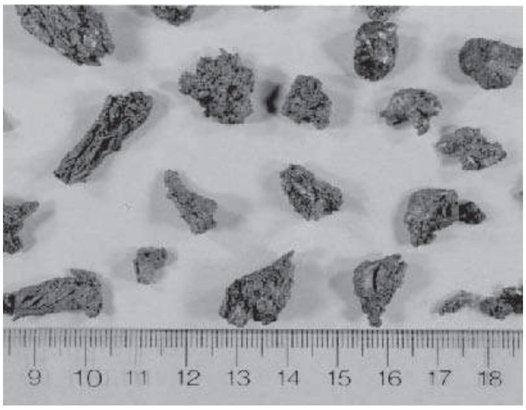


Fig. 3.4. Low magnification photo showing individual sponge particles (courtesy J. A. Hall)

The cost of producing titanium sponge can be conveniently separated into five components or cost elements. These are labor, equipment maintenance, utilities, and the two main ingredients (Mg and $TiCl_4$). A pie chart is shown in Fig. 3.5 that identifies the relative contributions of each of these elements to the overall cost. It can be seen that $TiCl_4$ comprises more than 50% of the cost, so efforts aimed at reducing the cost of titanium sponge must address this matter.

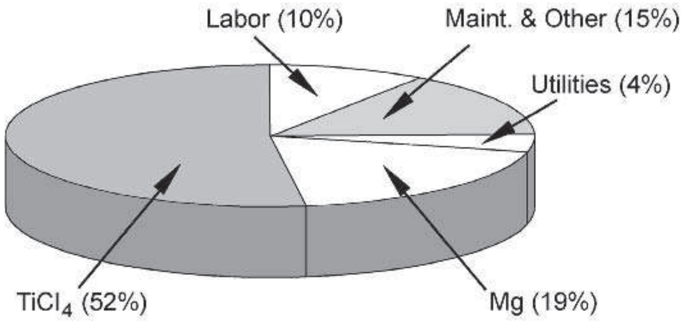


Fig. 3.5. Relative proportions of major cost elements for titanium sponge production (courtesy J. A. Hall)

Other processes for producing metallic titanium have been under investigation for years. Most of these have been directed to reducing the cost of sponge, generally without economic success. Electrolytic production (also called electrowinning) of titanium is one example that appears attractive and in the 1975-1985 time frame Dow-Howmet successfully demonstrated a pilot scale operation in the USA [3.3]. The down market for titanium at this time resulted in a decision not to proceed to full-scale operation. Consequently, the practicality of sustaining a reliable and affordable operation of a large capacity electrolytic reduction cell has not been demonstrated. The issues that remain to be demonstrated are the ability to seal a large cell in order to maintain a pure operating environment and the long-term stability of the electrodes.

Other recent efforts to produce very high purity titanium by electrolytic refining have been quite successful, both technically and economically [3.4]. Electrolytic refining starts by dissolving lower purity titanium in an electrolyte and redepositing it as high purity titanium. Through careful control of the deposition conditions and electrolyte purity a very high purity product can be obtained. This high purity metal is made into sputtering targets for use in electronic device fabrication. The economic success of electrolytically refined titanium is because the users of this high purity material use relatively small quantities in high value products, so the economics are completely different from structural applications.

There is a new process for making titanium sponge that is currently under intensive investigation. This process is known as the Electro-Deoxidation Process (EDO)^{TM} [3.5]. The EDO process converts a pressed and sintered TiO_2 cathode to titanium in situ by electrolytically separating the oxygen from the titanium ions using a molten $CaCl_2$ bath and a graphite anode. This leaves porous metallic titanium in place of the original cathode. In principle, this process also has the capability to make pre-alloyed sponge if oxides of the desired alloying elements are blended into the oxide cathode and are electrolytically reduced along with the TiO_2. While the results obtained using this process are quite limited and the potential for scale up is still a matter of analysis and subsequent demonstration, the potential for such a process is exciting for several reasons. First, the ability to make pre-alloyed sponge would permit elimination of the sponge and master alloy blending and mechanical compaction steps used to form a first melt electrode for ingot metallurgy melting, as described in Sect. 3.2.1. This may result in significant cost savings. Second, the ability to introduce alloying elements into titanium (e.g. W, Cu) that are difficult to introduce using conventional ingot metallurgy practice as discussed later. This new process opens a number of alloy synthesis options that have not been previously explored because of the melting constraint. The EDO process has been proven to be technically feasible but there are many details ranging from repeatability to product cost after scale up that require detailed study and analysis. Because it is somewhat revolutionary in its capability, the EDO process is mentioned here even though it's future as a commercial reality is still unclear.

3.2
Melting

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. This process is commonly referred to as "melting", but the resolidification of the molten metal is the key to obtaining homogeneous, high quality ingots for conversion to mill products.

A significant portion of this section is devoted to the discussion and characterization of melt related defects. These defects must be minimized for titanium to perform at a level that justifies its cost. It is because of the potential for these defects to be formed and the severe consequences of their presence that the elaborate and expensive methods are used to melt titanium and produce ingots. While the cost of preventing these defects is high, this strong, lightweight material would not be available for the most demanding applications if these defects could not be eliminated. The detailed nature of the defects is discussed later in Sect. 3.2.3, but it is useful here to outline the types of possible defects to emphasize the reasons for the approach that is taken for melting titanium. There are five principal types of defects in titanium. The primary source of these is melting. There are interstitial stabilized defects, known as type I defects or referred to as high interstitial defects (HIDs), tungsten rich inclusions, known as high density inclusions or HDIs, alpha stabilizer rich regions called type II defects, beta stabilizer rich regions called "beta flecks", and voids that occur during the solidification of the ingot. In contrast to other classes of metallic materials, where melting is used to eliminate defects, melting can introduce defects in titanium. Once formed, these defects can be difficult to eliminate through all subsequent processing steps, including remelting. In all cases, the entire spectrum of causes of these defects is not understood and the severity of the performance degradation associated with their presence is different for each type, as will be discussed later in this section. Table 3.1 is a summary of the types of known defects in titanium and some of their possible causes.

Molten titanium is very reactive, therefore, special means are required to produce ingots of both unalloyed titanium (CP titanium) and the various titanium alloys. Titanium and its alloys are melted either in a vacuum arc remelt (VAR) furnace or in a cold hearth melting (CHM) furnace. In either case, the melting is done in a manner that prevents molten titanium from contacting furnace refractories such as those used in vacuum induction melting furnaces or from being exposed to air. Production of titanium and titanium alloys has been done by vacuum arc melting since titanium has been a commercial product. Cold hearth melting has only become commercially feasible for rotor grade titanium since about 1985.

Table 3.1. Melt related defects known in titanium and their possible causes

Defect Type	Possible Causes
Type I ("Hard Alpha"), also called High Interstitial Defect (HID)	Sponge production – Fires during handling or shearing First melt electrode production – Fires during compaction – Improperly conditioned scrap – Contaminated master alloy – Contamination during welding Melting and remelting – Small water leak – Air leak – Aggressive grinding during ingot conditioning
High Density Inclusions (HDIs)	Scrap additions – Tungsten welding electrodes – Tool bits mixed into turnings
Beta Flecks	Melting segregation Conversion too close to transus (including adiabatic heating effects)
Type II (Alpha Stabilized)	Improper final melt phase (excessive pipe formation) Improper ingot top removal Al-rich "drop-ins" during EBM
Voids	Incorporation of shrinkage pipe during conversion Improper conversion practice

3.2.1
Vacuum Arc Remelting (VAR)

Vacuum arc remelting is actually a misnomer in that it is the initial melting process used in the production of titanium. This is in contrast to the production of nickel base alloys and specialty steels where the first melt process is vacuum induction melting, followed by vacuum arc remelting. Vacuum arc remelting is the most commonly used process for making titanium, but the use of cold hearth melting is growing as will be described later. Over time, the vacuum arc remelting process has been used to successfully make larger and larger ingots. The ingot size (diameter and weight) has increased due to the improved capability of melting larger diameter ingots of CP titanium grades and alloys such as Ti-6Al-4V. Larger ingots are more economical because losses during conversion of the ingot to the final product are smaller and the melting time including reloading of the furnace is shorter. Both of these factors plus minimizing the number of VAR units required for production result in lower product cost. Today, it is common to melt ingots of these materials as large as about 100 cm in diameter and weighing as much as 10 000-15 000 kg. Other titanium alloys are more difficult to melt because of a higher propensity for alloy element segregation during solidification leading to both beta flecks and type II defects. The minimization of beta flecks occurs if the segregation prone alloys are produced in smaller ingots, which impacts material costs. Type II defects are avoided by a melt practice that eliminates or minimizes shrinkage pipe at the ingot top.

The vacuum arc melting begins with a first melt electrode that is made up of mechanically compacted blocks of sponge and alloying elements, where each block has the desired nominal alloy composition. Sponge and alloying elements are blended together in a twin cone blender. This mixture is then placed in a die and mechanically compacted at room temperature into blocks using a hydraulic press. The as-compacted blocks have adequate “green strength” to remain intact during handling and melting. These blocks are welded together in an inert gas welding chamber to create the first melt electrode or “stick”. Because of the high cost of winning titanium, there is a strong economic incentive to recycle and reuse titanium scrap (often called revert) by reincorporating it into ingots during melting. This reuse is accomplished in unalloyed grades and non-rotor alloys by adding scrap of the same composition to this electrode during the electrode welding operation. This scrap is carefully controlled with regard to its origin and cleanliness. For example, the use of scrap that has been flame cut is generally not allowed. This is because experience has shown that the N and C enriched regions along the flame cut edges are not always refined out during melting. This can leave interstitial stabilized defects in the final product. Turnings generated during the machining of titanium parts are also used in the electrode make-up, but these also 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 broken WC cutting tools or other high density inclusions that can end up in the ingot. The usage of revert material is limited for various applications by different specifications. A picture of a first melt electrode is shown in Fig. 3.6. This figure shows the individual briquettes of compacted sponge and master alloy and the titanium straps that are welded to them to hold the electrode together during the first vacuum arc melt. This electrode is held in the VAR furnace by a stub. A stub configuration can be seen in Fig. 3.6 at the left. Once the first melting operation is complete, the ingot is removed from the copper mold. Figure 3.7 shows a large titanium alloy ingot after the VAR process is complete. Beside the ingot on the right is the vacuum jacket for the VAR furnace which is about 125 cm in diameter. This ingot is inverted and melted again.

Rotor grade VAR materials are typically triple melted so the ingot is once again inverted and the remelting process is repeated a second time in this case.

Fig. 3.6. First melt VAR electrode with welded individual briquettes and the stub on the left (courtesy RMI)

Fig. 3.7. VAR ingot (on left) after first melt (courtesy J. A. Hall)

VAR production of homogeneous, sound ingots of titanium alloys requires care and the detailed melting procedure depends on the particular alloy. Over the past 30 years dozens of improvements have been made to the process, some major and some minor. All of these have been directed toward reducing the possibility of defects and the extent of variation in the ingots. Figure 3.8 shows schematically the VAR process. This figure shows the VAR furnace, the electrode being melted, and the water-cooled copper crucible containing the new ingot with the molten pool at its top. In the figure the molten pool at the top of the new ingot is inside the solid line drawn near the top of the new ingot. There are a number of parameters that must be monitored and controlled during the final melting operation. This is required to ensure homogeneity and soundness of the ingots. Important parameters that require attention and that are often monitored during melting include the following:

- The vacuum in the furnace is continuously monitored as this ensures that no air or small water leaks are occurring to contaminate the melt with nitrogen or oxygen (major water leaks create a serious explosion hazard).
- The melt rate is continuously adjusted to control the size of the molten pool at the top of the ingot (see Fig. 3.8). The propensity for freezing segregation to occur varies with alloy type. The melt rate and molten pool depth are controlled accordingly. This is largely based on experience. In segregation prone alloys such as Ti-17 or Ti-10V-2Fe-3Al, it is common to reduce the ingot diameter to about 75 cm and melt at lower rates (5-6 kg/min versus 8-10 kg/min). This modified melt practice creates a smaller, shallower molten pool at the top of the ingot. The lower melt rates use correspondingly lower power settings (200-275 versus 400-500 kVA).
- Most VAR furnaces are equipped with electrical coils at the top of the ingot mold that create an electromagnetic field used to stir the molten metal. This is done to achieve improved ingot homogeneity. The extent to which stirring is employed varies between titanium producers and between alloys. There is no general agreement on the benefit it produces or, even, the extent to which it is necessary.
- As the final part (25-35%) of the ingot is approached, the melt rate is reduced by reducing the power in several steps. In the VAR process this is the same as the hot topping operation practiced during conventional ingot metallurgy melting of Ni or Fe base alloys. This procedure minimizes the extent of shrinkage pipe formation and other defects such as type II at the ingot top. Minimization of shrinkage pipe reduces the loss of metal during conversion and helps eliminate defects that can be created when this pipe is inadvertently incorporated into the product.

The techniques used to control melting are quite empirical and are equipment dependent. Consequently, there is a significant “art” content involved in the melting operation. This makes experienced melt furnace operators (known as “melters”) a valuable resource to all titanium producers. Eventually, the use of better process controls coupled with knowledge based systems may eliminate this dependence on individuals with a great deal of experience.

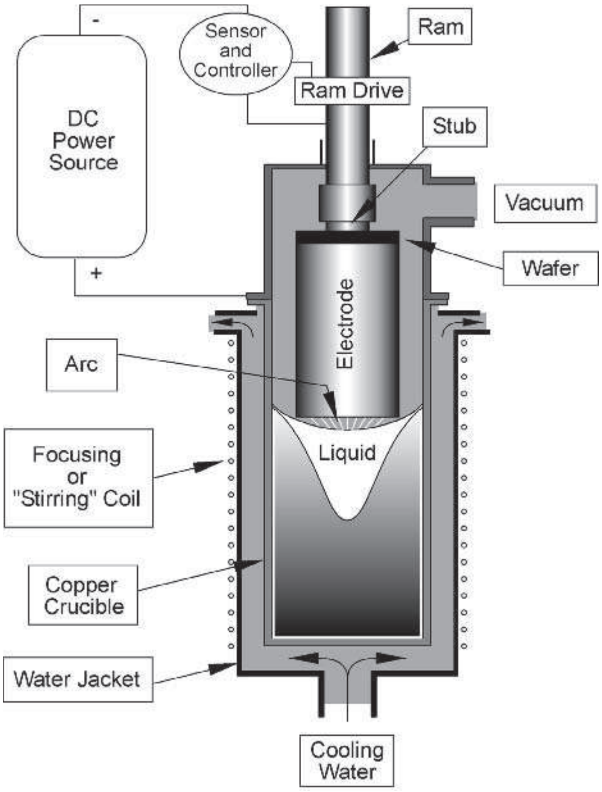


Fig. 3.8. Schematic of VAR furnace and ingot during a second melt, the electrode being remelted is at the top and the new ingot is at the bottom (courtesy J. A. Hall)

3.2.2
Cold Hearth Melting (CHM)

Cold hearth melting (CHM) is a newer melting method that seems to have several advantages over the VAR process for rotor grade material [3.6, 3.7]. A schematic of a cold hearth furnace is shown in Fig. 3.9. This method utilizes a water cooled copper vessel (the hearth) which contains the molten titanium. Cold hearth melting is conducted in either a plasma arc or an electron beam melting furnace. In both cases, the heat input from the heat source (the electron beam or the plasma torch) 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 cold hearth melting 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. In principle, this creates the opportunity for refining the alloys through dissolution of any nitrogen or oxygen rich defects without incurring a large, deep molten metal pool as in the VAR process that can cause solute segregation.
- It automatically introduces gravity separation of high density inclusions such as WC tool bits or tungsten welding electrode tips that are introduced along with the revert. The high density inclusions become trapped in the mushy zone of the skull and are not transmitted to the ingot. This is in complete contrast to the VAR process, where all of the material in the electrode ends up in the ingot.
- It allows direct casting of non-axisymmetric 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 a particularly attractive method for making sheet and strip from alloys that are readily rolled into coil without reheating. Of special interest are the various grades of CP titanium listed in Table 2.6.
- As noted earlier, the cost of titanium is a deterrent to its expanded use. Cold hearth melting is the most efficient method for reusing all forms of revert.
- In contrast to the physical environment in the VAR furnace chamber, the cold hearth furnace is more conducive to the use of online sensors. Consequently, this process is more amenable to real-time process controls and detection of process variations during the melting process.

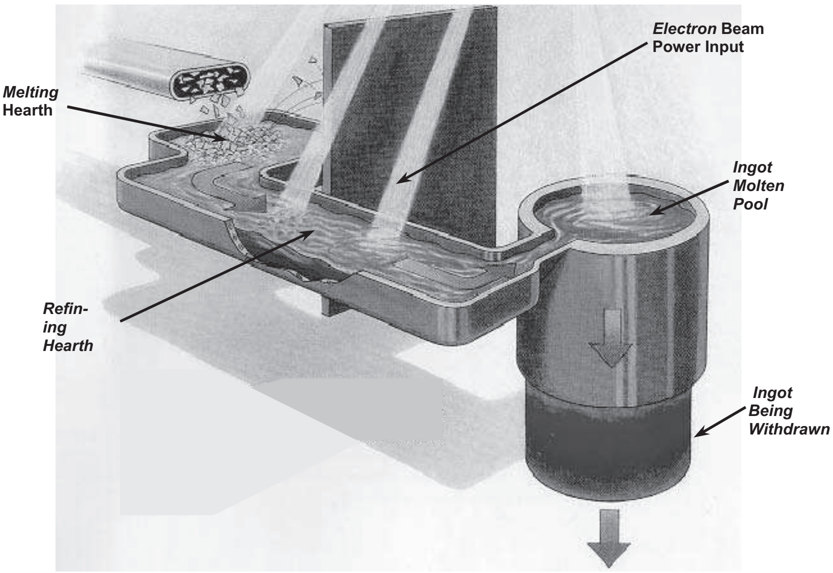


Fig. 3.9. Schematic of the hearth in an electron beam melting furnace (courtesy THT-TIMET)

There are two types of cold hearth melting furnaces in use today. One uses plasma arc melting (PAM) technology and the other uses electron beam melting (EBM) technology. These furnaces obviously differ in heat source (plasma torches vs. electron beam guns). Also, electron beam melting furnaces operate in vacuum, whereas plasma arc melting furnaces operate in a partial pressure of argon. Apart from these differences, the remaining physical arrangements of these furnaces are very similar. Production cold hearth melting furnaces are typically large. Figure 3.10 shows a man standing atop the vacuum chamber that contains the hearth of an electron beam melting furnace. This furnace is capable of melting about 10^6 kg of titanium per year.

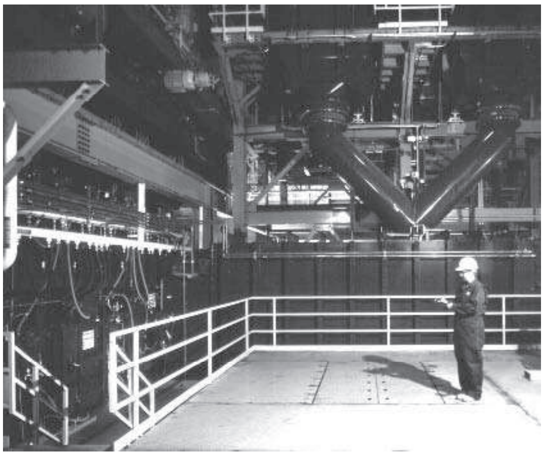


Fig. 3.10. Electron beam cold hearth furnace showing the size of such facilities (courtesy Teledyne Allvac)

The overall hearth in a cold hearth melting furnace usually consists of several compartments, Fig. 3.9. From Fig. 3.9, it can be seen that the input material is fed into the first chamber (the melting hearth) where the energy from the heat sources melt it. These heat sources are continuously moved or scanned over the surface of the molten pool. In plasma arc melting furnaces, the torches are physically reoriented whereas in electron beam melting furnaces, the beam is redirected by electromagnetic deflection coils. This scanning of the heat sources is done under computer control, which optimizes the uniformity of the molten pool surface temperature, for example by compensating for heat loss into the water-cooled copper hearth at the pool edges. The number of electron guns or plasma torches, the heat input, and the scan patterns are alloy and furnace dependent. Once molten, the titanium alloy flows over a weir or dam into the first refining hearth where another array of heat sources maintains it in the molten state. The molten alloy then flows over a second weir into the second refining hearth where another array of heat sources keeps it molten and permits further refining. The molten alloy finally flows over the exit lip of the second refining hearth into an ingot mold. In the current example the ingot is round, but rectangular shapes also can be directly cast as previously mentioned. A large rectangular slab from an electron beam cold hearth melting furnace is shown in Fig. 3.11. This slab weighs approximately 12 000 kg. The principal disadvantage of cold hearth melting is the relatively smaller superheat that can be achieved in the molten alloy as it enters the mold, compared to the VAR process. Here, superheat is defined as the ΔT of the molten alloy above the liquidus temperature. This leads to a rougher ingot surface (roughness also is called wall quality) which can lead to increased conditioning requirements and added cost compared to VAR. In the case of slab casting, the geometric advantage of the shape for flat rolled products overwhelms any penalty due to ingot wall quality.

Fig. 3.11. Large titanium slab directly cast from a cold hearth melting furnace (courtesy Teledyne Allvac)

During the time the molten metal is in the two refining hearths, there is a significant opportunity to remove any interstitial stabilized inclusions by dissolution in the molten titanium alloy (ergo alloy refining). A thermodynamic driving force exists for this dissolution, however, the kinetics are relatively slow. Thus, the promise of complete refining (removal) of unwanted interstitial stabilized inclusions by cold hearth melting has not been realized. It is clear that refining does occur, but the required residence time in the hearth to achieve complete refining of relatively large inclusions would make the cold hearth melting process economically unattractive. It is clear, however, that cold hearth melting does allow complete removal of high density inclusions (HDIs). This is a major benefit of cold hearth melting of rotor grade material. This is particularly true during periods when titanium is in short supply, so there is a strong incentive to reuse all available turnings. Increased turning use increases the probability of having HDIs present even in rotor grade materials. Extensive production experience, supported by modeling, has shown that HDIs are not carried along over the weirs and into the ingot in the cold hearth melting case. This is because the density differences between titanium and the HDIs cause them to sink and stick in the mushy zone between the solid skull and the molten alloy.

Current cold hearth melting practice for rotor grade alloys requires application of a final VAR step to the ingot after it is produced in a cold hearth melting furnace [3.8]. This is because both electron beam and plasma arc ingots made by cold hearth melting can have process related defects that must be removed to qualify the material as rotor grade. In the electron beam melting process, aluminum evaporates from the melt and deposits on the cold roof and walls of the furnace vacuum chamber. These can drop into the melt at the latter stages of melting and result in Al-rich regions that are not adequately homogenized before solidification. The final VAR step re-homogenizes the alloy. In the plasma arc melting process, small inert gas bubbles from the argon ion plasma are formed in the molten metal and are trapped in the ingot. Since argon is essentially insoluble in titanium, these bubbles remain as pores. The final VAR step allows these bubbles to escape. There are two incentives to eliminate the final VAR operation, one is economic and the other is concern that this step creates an opportunity to reintroduce interstitial stabilized inclusions if a vacuum or water leak or other melt furnace malfunctions should occur. It appears that the most promising means of achieving this objective is with a partial pressure plasma arc melting process. Under such melting conditions, evaporation and condensation of aluminum is minimized and the partial pressure allows elimination of the argon filled pores. Realization of this goal is a number of years away because of the necessity of producing substantial quantities of material and inspecting it to statistically establish confidence in the “hearth only” process capability. Until qualification for rotor grade, the material produced by an unapproved melt practice must be used for non-rotor applications. There are many noncritical applications for some alloys such as Ti-6Al-4V and none for others such as Ti-17 or Ti-6246. Consequently, the qualification procedure for Ti-6Al-4V is more affordable because the material made during qualification can be sold for these non-rotor applications. This minimizes the nonrecurring cost of this qualification procedure by allowing all except the incremental cost of the CHM process to be recovered through the sale of the product made during the qualification process. Thus, there is an added economic penalty for qualifying a new CHM source for Ti-17 or Ti-6246. This added economic penalty extends the time required to achieve qualification and complicates the qualification process.

3.2.3
Melt Related Defects

Frequent reference already has been made to melt related defects in titanium alloys (Table 3.1). Experience has shown that, once formed, these defects are very difficult to eliminate and can have an extremely detrimental impact on material performance. Consequently, a separate section is devoted to the subject of melt related defects.

Melt related defects can be categorized as either intrinsic or extrinsic, depending on their origin. Extrinsic defects are caused by inadvertant introduction of impurities during the preparation of the electrode or during the melt process. Intrinsic defects are those that can be present if the ingot solidification occurs without proper control. The nature and origin of melt related defects in VAR material are discussed in [3.9].

As previously mentioned, the solidification of titanium ingots must be controlled to ensure homogeneity. The degree of difficulty involved in achieving homogeneous solidification depends significantly on the alloy. Those alloys that contain β eutectoid forming elements, such as Fe, Cr, Mn, Ni, and Cu, typically have depressed freezing temperatures resulting in solidification over a significant temperature range. This situation can lead to solute segregation during ingot solidification. The most common source of depressed freezing is a eutectic reaction in the (liquid+solid) portion of the phase diagram, such as in the Ti-Fe, Ti-Mn, and Ti-Cu systems. The Ti-Fe phase diagram is shown as example in Fig. 3.12. The presence of the eutectic extends the freezing range of the alloy and causes the last liquid to solidify to be enriched in solute. This creates the possibility of long range solute segregation during ingot solidification. Alloys that only contain β isomorphous alloying additions, such as Mo, V, and Nb, do not have similar depressed solidification temperatures and these alloys are much less prone to freezing segregation (see Ti-Mo phase diagram in Chap. 2, Fig. 2.12). Segregation of Fe or Cr during freezing results in regions that have a lower β transus temperature. These regions exhibit a different microstructure than 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”. An example of a beta fleck in the alloy Ti-10V-2Fe-3Al is shown in Fig. 3.13 [3.10]. Here the large β grains and the lower volume fraction of α precipitates within the beta fleck are clearly visible. Beta flecks are the direct result of remaining alloying element freezing segregation. The segregated areas typically occur on a scale ranging from a few hundred micrometers to a few millimeters. These solidification related defects can occur in any titanium alloy but, as mentioned earlier, alloys containing eutectoid forming elements, such as Cr, Fe, or Ni, are considerably more susceptible to the creation of beta flecks. These beta flecks shown in Fig. 3.13 are detrimental to the fatigue strength because they are weaker and deform preferentially leading to early crack nucleation.

The reactivity of titanium also 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, therefore, are 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. A nitrogen stabilized type I inclusion in a forging is shown in Fig. 3.14a. Because of the propensity to crack at low strains, the presence of a type I inclusion can seriously decrease the fatigue capability of the material. Thus, great care is taken to minimize their occurrence. 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. This has reduced the frequency of these defects by 10 to 100 times. Today, the frequency of type I defects detected in rotor grade titanium alloys is less than one defect per every 500 000 kg of material melted. Since the aircraft engine industry uses over 1 000 000 kg of titanium alloys each year this means that defect detection and elimination after melting is still essential. The most effective inspection method is ultrasonic inspection. This will be described in greater detail later in Sect. 3.8. Here, it is important to mention that the basis for ultrasonic detection of type I defects is the void that usually accompanies the defect, as can be seen in Fig.3.14a. The cause of this void is the strain incompatibility between the matrix and the rigid type I inclusion. The reduced ductility of the nitrogen rich region of the matrix adjacent to the inclusion may also be a factor, depending on the temperature at which the strain is introduced. 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 also will detect regions of texture or preferred orientation and lead to many false calls during ultrasonic inspection. Causes of “false calls” are discussed in Sect. 3.8.1. Disposition of false calls consumes time and resources and is a significant factor in adding cost to the production of rotor quality material.

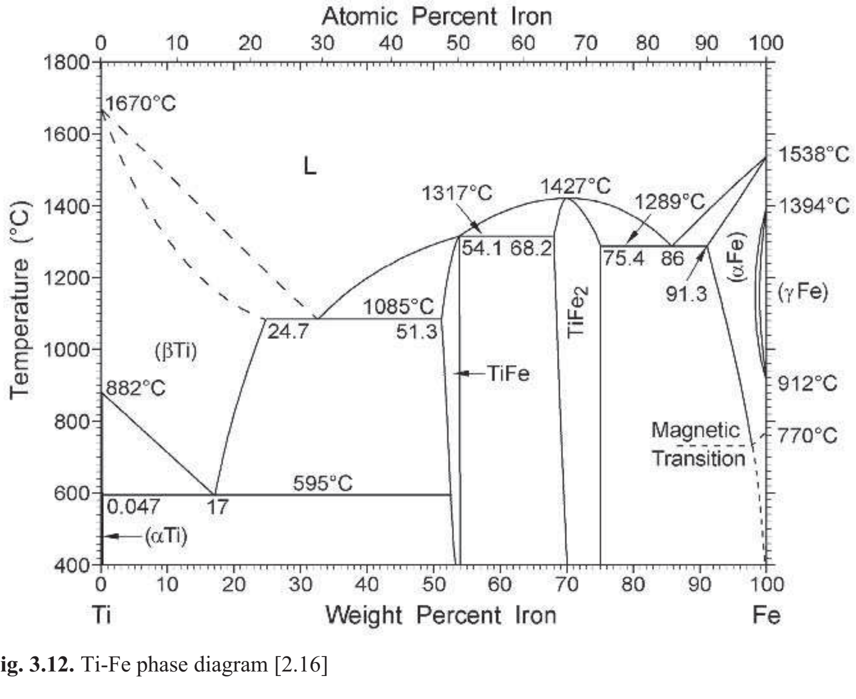


Fig. 3.12. Ti-Fe phase diagram [2.16]

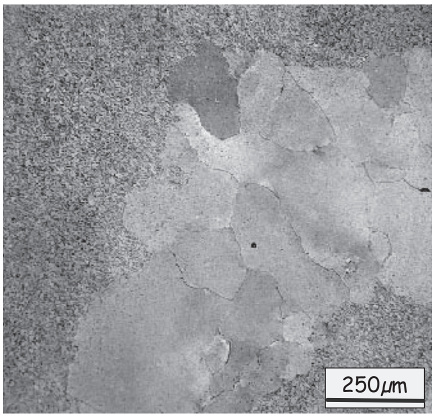
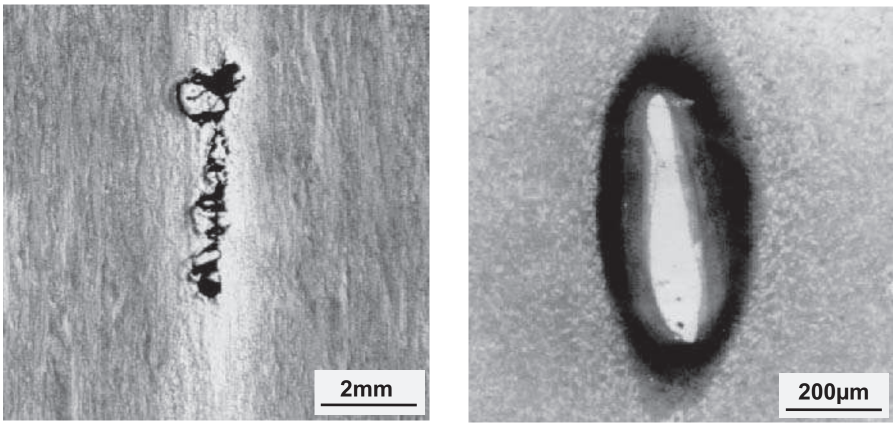


Fig. 3.13. Fe enriched region, known as beta fleck, in Ti-10V-2Fe-3Al, LM (courtesy R. R. Boyer, Boeing)



a **b**

Fig. 3.14. Melt related defects in Ti-6Al-4V forgings, LM: (a) Type I nitrogen stabilized inclusion (b) High density, tungsten rich inclusion (courtesy C. E. Shamblen, GE Aircraft Engines)

There also is another melt related defect that is Al-rich and usually is a result of incorporation of Al-rich regions from the shrinkage pipe near the top of the ingot into the product. These Al-rich regions are known as type II defects. Type II defects are less detrimental to properties than type I defects, but in high strength alloys such as Ti-17, these defects do not respond to heat treatment (aging) as much as the surrounding matrix and 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 by cropping the portion at the ingot top that contains the shrinkage pipe so it does not appear in the product.

Alloy segregation effects (beta flecks and type II defects) also can be minimized by ingot homogenization.

It has been mentioned that the use of titanium turnings is a common means of recycling titanium and is done to reduce the cost of the product and to increase the available quantity of titanium alloys. This is particularly helpful during periods when the titanium demand is high relative to capacity. Other types of scrap than turnings and the mill scrap internally generated by the titanium producer are also used. For example, pieces of sheet and plate generated by fabricators of titanium equipment, e.g. heat exchanger, also are separated by grade and reused. One of the issues that the reuse practice creates is the possibility that tungsten rich, high density inclusions (HDIs) can be introduced into the product. These tungsten rich inclusions can come from two principal sources: tungsten inert gas (TIG) welding electrodes that are embedded in welds and WC from broken tool bits. The high melting temperature of tungsten and WC make these inclusions relatively stable during vacuum arc melting and subsequent remelting. Thus, they are incorporated into the ingot with little or no modification. An example of a WC inclusion in a titanium alloy forging is shown in Fig. 3.14b. The dark etching matrix adjacent to the inclusion contains fine α precipitates in the β phase. This β phase is enriched in W due to diffusion.

The use of scrap, or revert as it is often called, including turnings varies widely by alloy, by material grade, and by user specification. The various engine manufacturers have different permissible levels of turnings that can be used in rotor grade material ranging from none to as much as 50%. Other (non-rotor) grades have more liberal allowances and CP titanium has no limitation. The incorporation of turnings and revert into an ingot is considerably easier and more economical in the case of cold hearth melting, because they can be fed directly into the melting hearth without prior consolidation.

This discussion of titanium alloy melting shows the complexity of producing commercial quantities of mill products from reactive materials for high performance applications. Significant technological advances have been made over the past 40-50 years in which titanium alloys have been in existence as commercial products. While the processes still can be improved, the reliability of titanium components, as affected by melt practice, has increased greatly. This improvement is an ongoing effort. The value of continuous improvement must be recognized by both users and producers.

3.3
Primary Processing

Once the ingot is melted and 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 use 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 hours. It is important to emphasize that homogenization does not remove HDIs and type I (hard alpha) defects.