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Titanium production for aerospace applications

Abstract: *Titanium parts are ideally suited for advanced aerospace systems because of their unique combination of high specific strength at both room temperature and moderately elevated temperature, in addition to excellent general corrosion resistance. The objective of this work is to present a review of titanium metallurgy focused on aerospace applications, including developments in the Brazilian production of titanium aimed at aerospace applications. The article includes an account of the evolution of titanium research in the Brazilian Institute (IAE/CTA) and the current state-of-art of titanium production in Brazil.*
Key words: *Titanium, Aerospace industry, Powder metallurgy.*

INTRODUCTION

Over the last decade, the focus of titanium alloys development has shifted from aerospace to industrial applications. However, the titanium industry continues to depend on the aerospace market and this sector will constitute a significant percentage of total consumption for years to come. The metallurgy of titanium and Ti-base alloys has been intensely researched over the last 50 years. Titanium has unique properties such as its high strength-to-weight ratio, good resistance to many corrosive environments and it can be used over a wide range of temperatures. Typical engineering applications of titanium alloys include the manufacture of cryogenic devices and aerospace components. The high buy-to-fly ratio associated with many titanium components, combined with forging and machining difficulties, has led to a strong drive for near-net titanium manufacture. A very promising method of attaining this goal is powder metallurgy (P/M) (Froes, 1980).

The primary justifications for using titanium in the aerospace industry are (Boyer, 1994):

- weight savings (primarily as a steel replacement);
- space limitation (replace Al alloys);
- operating temperature (Al, Ni, steel alloys replacement);
- corrosion resistance (replace Al and low alloy steels); and
- composite compatibility (replace Al alloys).

Weight savings are due to the high strength-to-weight ratio. The lower density of titanium compared with steel permits weight savings, replacing steels even though they may be higher strength. As the strength of titanium alloys is significantly higher than Al alloys, weight savings can be achieved when they their replace aluminum despite the 60 per cent higher density, assuming that the component is not gage limited (Allen, 1996).

Titanium could also replace aluminum when the operating temperature exceeds around 130C, which is the normal maximum operating temperature for conventional aluminum. These conditions exist, for example, in the nacelle and auxiliary power unity (APU) areas and wing anti-icing system for airframe structures. Steel and nickel-based alloys are obvious alternatives, but they have a density about 1.7 times that of titanium (Andersen, 1980, Donachie, 1988).

Corrosion resistance can be a very important issue. The corrosion resistance of titanium is such that corrosion protective coatings or paints are not required: (paint is applied when titanium comes into contact with aluminum or low alloy steel components to prevent galvanic corrosion of the contact material). Much of the floor support structure under the galleys and lavatories is in a very corrosive environment that dictates the use of titanium to provide high structural durability (Andersen, 1980).

Polymer matrix composite (PMC) compatibility is becoming a bigger issue with increased use of composite structures on aircraft. Titanium is galvanically compatible with the carbon fibers in the composites, whereas aluminum (and low alloy steels) and carbon generate a significant galvanic potential. The choice of titanium in these instances is related to the criticality of the structure (Boyer, 1994).

Titanium is not as widely used as aluminum or steel but it is not a rare or precious metal. Titanium is the fourth most abundant metal in the earth's crust (0.86 per cent by weight) after aluminum, iron, and magnesium. However, titanium is difficult to extract from its core, difficult to process, and difficult to manufacture. Just accounting for the extraction and processing costs to produce an ingot, titanium is ~30 times more expensive than steel and ~6 times the cost of aluminum (Hurless, 2002).

Historically, titanium has experienced anemic growth when compared with aluminum and stainless steel alloys.

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The high cost of production limited the use of titanium to applications requiring high performance or where life cycle cost analyses justified its use. The aerospace and defense communities stimulated initial development of titanium alloys in the early 1950s. Aircraft development during the Cold War was performance-driven without much regard to cost. A radical example of this was the SR-71 Blackbird reconnaissance aircraft, with over 90 per cent of the structure being titanium (Hurless, 2002).

The growth potential and cost-cutting initiatives of titanium were severely limited by the dependence upon the cyclic nature of the aerospace industry, with the market experiencing 4-5 year cycles of boom and bust. During boom periods, users were only interested in rapid access to materials, leaving reduced time for development of low cost techniques; bust periods had few resources available for low cost techniques (Hurless, 2002). Cost-conscious markets, such as the automotive industry, are reluctant to commit to titanium because of the unpredictability of the cost fueled by the boom and bust economics. However, with world production of 60 million vehicles annually, even 0.5kg of titanium in 50 per cent of the vehicles produced would increase titanium use by 30 per cent, helping to stabilize the cost and reduce dependence on the aerospace industry (Andersen, 1980).

Every stage of titanium production except the mining of ore has a tremendous potential impact on the final cost of titanium products. Regarding ore mining, the cost of ore is highly dependent on demand, thus cost reductions will naturally result from a major increase in the demand for titanium products. When considering cost reduction, it is strategic to focus on the early stages of production, where any cost advantages achieved would be carried through all production stages. The cost of extracting titanium from the ore is approximately 20 times that of steel on a 1-to-1 weight basis, but roughly 11 times when accounting for the density advantage of titanium (less titanium would be required to perform the same function as steel) [6].

Beyond that, machining costs for titanium are generally significantly higher than for the other materials (at least 10 times higher than to machine Al). In that sense, titanium alloy production using powder metallurgy (P/M), starting from the elemental or prealloyed powders is a interesting route considering its lower costs, versatility and also the facility it offers to manufacture parts with complex geometry and close to the final dimensions (Henriques 2005, Froes, 1988).

The Kroll Process

The basic chemical process for titanium production was patented by Wilhelm Kroll in 1938. The Kroll process has four stages: tetrachloride ($TiCl_4$) production, reduction reaction, vacuum distillation, and melt purification. The first step in the process is the preparation of the tetrachloride itself, which is carried out by the chlorination of a mixture of carbon with rutile or ilmenite in a fluidized bed furnace. The reduction reaction is carried out in a large retort, in an inert atmosphere, where titanium tetrachloride is sprayed onto a high-temperature reactive surface of molten magnesium. $TiCl_4$ reacts to form a sintered, porous mass of titanium, salt, and unreacted chemicals called "sponge" (Kroll, 1937). After the reaction reaches its equilibrium state, the residual impurities are eliminated by a vacuum distillation stage. One end of the retort is cut off and the sponge is jacked out of the retort. It is then chopped and ground into chips of about one centimeter size. The chips are acid-leached, water-washed, and dried. In the final stage, the chips are compressed and welded into an electrode, which in turn is melted into an ingot in a vacuum arc furnace. Alloys of titanium are formed by adding chips of the alloying elements to the electrode as it is being compressed and welded into an electrode shape. The arc melting removes volatile impurities and improves homogeneity. High purity alloys require an initial melt and two further remelts [Kroll, 1940].

The Kroll process has a number of serious disadvantages [Collings, 1983]:

- It is a multi-step process.
- Each individual step is a batch process.
- The initial stage operates at high temperature in retorts with short working lifetimes.
- It produces a sintered product with high levels of impurities.
- The second stage removes some of the impurities and discharges a polluted waste stream.
- The purification stage removes the rest of the impurities through multiple melts in high vacuum arc furnaces.

All of these inherent disadvantages add up to a product that is so expensive it can compete with other metals only in very specialized niche markets.

Titanium alloys

Titanium exists in two crystallographic forms. At room temperature (RT), unalloyed (commercially pure) titanium has a hexagonal close-packed (hcp) crystal structure referred to as alpha (α) phase. At 883°C (1621°F), this transforms to a body-centered cubic (bcc) structure known as beta (β) phase. The manipulation of these crystallographic variations through alloying additions and thermomechanical processing is the basis for the development of a wide range of alloys and properties. These phases also provide a convenient way to categorize titanium mill products (Barksdale, 1966).

There are three titanium alloy types based on the composition of the alloy and the resultant predominant room temperature constituent phase(s), and each of these families of alloys serves a specific role. The alloy types include alpha (α) alloys, alpha (α) + beta (β) alloys and (β) alloys. Alpha is the low temperature allotrope of titanium, and the microstructure consists predominantly of the α-phase. Alpha (α) + beta (β) are, for the main part, still mostly α at RT, but they do have more of the β-phase, the high temperature allotrope, than the former class of alloys. The definition of β-alloys is not fully agreed upon, but in very general terms, they are capable of retaining 100 per cent β when quenched from the β-phase field (Leyens, 2003).

Alpha alloys contain elements such as aluminum and tin. These α-stabilizing elements work by either inhibiting change in the phase transformation temperature or by causing it to increase. Alpha alloys generally have creep resistance superior to β alloys, and are preferred for high-temperature applications. The absence of a ductile-to-brittle transition, a feature of β alloys, makes α alloys suitable for cryogenic applications. Alpha alloys are characterized by satisfactory strength, toughness, and weldability, but poorer forgeability than β alloys. This latter characteristic results in a greater tendency for forging defects. Smaller reductions and frequent reheating can minimize these problems. Unlike β alloys, alpha alloys cannot be strengthened by heat treatment. They most often are used in the annealed or recrystallized condition to eliminate residual stresses caused by working. Ti-5Al-2,5Sn is the most important alloy and it is used for cryogenic applications (Barksdale, 1966).

Alpha + beta alloys have compositions that support a mixture of α and β phases and may contain between 10 and 50 per cent β phase at room temperature. The most common α + β alloy is Ti-6Al-4V. Although this particular alloy is relatively difficult to form even in the annealed condition, α + β alloys generally have good formability. The properties of these alloys can be controlled through heat treatment, which is used to adjust the amounts and types of β phase present. Solution treatment followed by aging at 480 to 650°C (900 to 1200°F) precipitates α, resulting in a fine mixture of α and β in a matrix of retained or transformed β phase Ti-6Al-4V is the most widely used titanium alloy and accounts for nearly 45 per cent of total titanium production (Lütjering, 2007).

Beta alloys contain transition elements such as vanadium, niobium and molybdenum, which tend to decrease the temperature of the α to β phase transition and thus promote development of the bcc β phase. They have excellent forgeability over a wider range of forging temperatures than α alloys, and β alloy sheet is cold formable in the solution-treated condition. Beta alloys have excellent hardenability, and respond readily to heat treatment. A common thermal treatment involves solution treatment followed by aging at temperatures of 450 to 650°C (850 to 1200°F). This treatment results in formation of finely dispersed particles in the retained β. Ti-10V-2Fe-3Al is one of the most important β alloys for aerospace applications nowadays (Hanson, 1995, Stephen, 1988).

Market

Since the attacks on the World Trade Center in September 2001, the titanium industry has been characterized by a steep decline in demand for its use in aerospace applications. Demand for titanium sponge in the USA, the world's largest market, fell by 34 per cent in 2002, and that for mill products by 30 per cent. The SARS (Severe Acute Respiratory Syndrome) crisis and the Iraq war prevented recovery in 2003 (Lütjering, 2007). However, in the absence of any further catastrophic events impacting directly on commercial airlines, demand for titanium metal is forecast to recover steadily over the next five years. The western world's passenger airline fleet of over 100 seats is expected to increase from 10,800 aircraft in 2004 to over 30,000 in 2020. This growth in demand will be boosted further by the increasing production of military aircraft, particularly with the F22 having probably the highest proportion of titanium of any aircraft, with 39 per cent by weight of titanium (Froes, 2004).

Russia, Kazakhstan and Japan dominate sponge production. Supply of titanium sponge is confined to nine producers in six countries. Russia, Kazakhstan and Japan now account for an estimated 75 per cent of world production (Fig. 1), which is around 73000t (Henriques, 2008). The role of Russian group VSMPO-Avisma in the titanium market continues to grow significantly with operational capacity reaching 24000t/year in 2004. A recent link up with Allvac (Allegheny Technologies) has also given them a much better base for selling in the USA, the largest consumer of titanium metal (Seong, 2009).

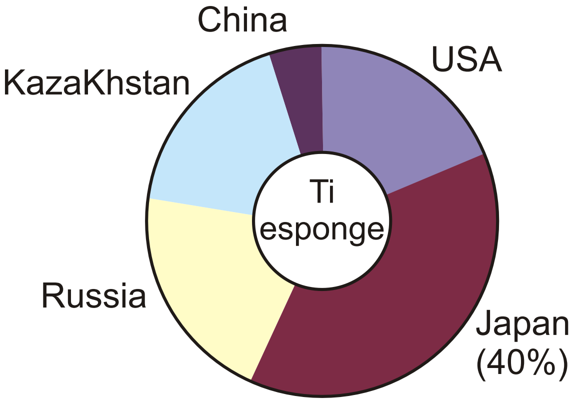


Figure 1: Market share of titanium sponge production (Seong, 2009).

The high cost of recovery discourages wider use. The use of titanium metal in cars, buildings and medical applications is currently restricted by the high costs of recovery and processing. Development of the FFC Cambridge continuous process for producing titanium sponge, which involves direct electrochemical reduction of TiO_2 in fused salt, nowadays, has funding from the US Department of Defense and commercialization appears to be closer. Similarly, other advances in powder metallurgy, laser forming and casting may reduce costs, but the expensive processes required to melt and alloy titanium will continue to reduce its competitiveness. Nevertheless, larger scale output of lower cost titanium and titanium alloy products for use in applications with broader tolerances, such as automotive parts and construction, remains a possibility (Rossman, 2007).

The use of titanium in aircraft is rising. The main end uses for titanium in aerospace are in compressor blades and wheels, stator blades, rotors, and other parts in aircraft gas turbine engines. The second largest end use is in airframe structures such as landing gear, ducting, wing-carry through structures, weight-and-space-critical forgings, and in structures where resistance to heat is important. The amount of titanium used per aircraft has increased steadily from the historical 10 per cent, with as much as 65t used in each Airbus A380.

The price of titanium grew 20 per cent in 2005, causing concern to the manufacturers of aircraft. Sponge producers had decreased production due to the reduction in demand in 2001. With the current growth of titanium use in the sector, prices are rising. The use in other applications such as power stations and desalinization units in China has contributed to the increase in prices (Seong, 2009). Titanium sponge which traditionally sold at 10 dollars/kg reached 30 dollars in 2005, with the price falling to 20 dollars in the middle of the year, later returning to 30 dollars by the end of the year. The development of the 787 Boeing and the Airbus A-380, which use large amounts of titanium, has contributed to the increase in demand. It is supposed that with the stabilization of the production, the trend is to return to normal values up to 2010 (Rossman, 2007, Roza, 2008).

Titanium Production in Brazil

Studies on metallic titanium production in Brazil were originally developed in the Military Institute of Engineering (IME), in 1965, as a result of undergraduate work, when two small blocks of sponge with about 2 kg each were produced. In the same year, the Brazilian Air Force (MAer) carried out its first study centered on the development of titanium production techniques, not only for use in aircrafts, but also aimed at creating conditions in Brazil for: the consumption of the metal; the exploration of Brazilian ores and the development of a new technology for the treatment with reactive metals. These research activities were pioneering in the use of vacuum equipment for the melting and refining of metals in Brazil, developed in the Materials Division of the Aerospace Institute (AMR/IAE/CTA) (Henriques, 2008).

AMR began its work with a view to supplying the needs related to ferrous and non-ferrous materials, used in structural parts of aircraft and rockets (Henriques, 2008).

The Metallurgical Processes Group (GPM) was created in 1965 in order to produce reactive metallic alloys, in particular, titanium and zirconium for the aerospace industry. To achieve these objectives, a laboratory with a complete infrastructure for vacuum melting and purification was created, including Vacuum Arc Remelting (VAR), Vacuum Induction Melting (VIM), Electro-slag and Electron Beam furnaces. This group of equipment was, at that time, the most expensive and capable research center plant in Brazil. The group generated an enormous amount of reports, articles, books and theses. During this time, GPM developed research lines in strategic materials such as zirconium, uranium, magnesium, beryllium, germanium, refractory alloys and especially titanium (Henriques, 2008, Rover, 1971a). These works are of immeasurable importance in the advance of the national research on strategic materials. GPM was a pioneer in the use of vacuum metallurgy for refining metals and for the production of reactive metallic alloys, being the generator of the most important special alloys producer in Brazil, Eletrometal (Henriques, 2008).

Historical importance of the Titanium Project

All the technology was developed with the aim of transferring it to Brazilian industry and the country was close to possessing an industry based on titanium and reactive metals. Titanium received huge investment from Brazil's federal government (Henriques, 2008). For Brazil, the Titanium Project was important for the following reasons: it provided acquisition of wide experience in the titanium, that culminated in the award of a patent, which received an important Brazilian Prize for innovation techniques in 1980; - Brazil became self-sufficient in titanium sponge production, in a process previously only available in a closed group of industrialized countries; it remains to this day the only successful experience in metallic titanium production in Latin America; it succeeded in placing on the Brazilian market a reasonable amount of Ti sponge (in the main program alone, around 30t was produced in the CTA); it promoted knowledge of the metallic chloride reduction technology and the production of reactive metals, such as zirconium, uranium, niobium and magnesium; and provided the necessary experience in vacuum metallurgy for the manufacture of reactive alloys and metal refining, generating the advance of the Brazilian industry (Henriques, 2008).

Historical facts about the Titanium Project

1965 - Studies at the CTA start with the elaboration of the first project backed by the National Bank of Development (BNDE);

1966 - Construction of the pilot-plant infrastructure; November - Signature of the contract with BNDE;

1967 - Start of the assembly of the pilot-plant equipment;

1968 - Inauguration of pilot-plant May - first operation of the $TiCl_4$ purification plant. Accident in the plant, with leaking of titanium tetrachloride from the distillation tank, causing the interruption of the unit; September - operation of the reduction plant;

1969 - May - restart of the $TiCl_4$ purification plant; June second operation of the reduction plant; July - operation of the reduction plant; August - first operation of the vacuum distillation plant; September second operation of the vacuum distillation plant.

1970 - 1972 - integrated operation of pilot-plant in order to introduce modifications to the original equipment aimed at the unification of the reduction and distillation plants; - operations on a scale of 100 kg of sponge;

1973 - 1976 Routine operation: - consolidation of the modifications. - Production of 200 kg of sponge; - End of main development works.
1977 - Patent Request to INPI;

1977 - 1978 - Transfer of the Titanium Project to VALEP (subsidiary of Vale do Rio Doce Company, CVRD);

1979 - Interruption of the negotiations;

1980 Negotiations with METAMIG;

1981 - Signature of agreement number: 02-IPD/81, between CTA and METAMIG;

1982 - Implementation of first work program with METAMIG;

1983 - 1985 - Interruption of the works due to financial problems with METAMIG; Negotiations with CVRD for the transfer of agreement number: 02- IPD/81;

1986 - Signature of the Additive Term number: 06-IPD/86, transferring agreement CTA/METAMIG to CVRD - Start of the work program with CVRD;

1987 - Finish of the work program with CVRD. End of titanium sponge production at the CTA.

Summary of the Titanium Project

All the goals of the agreement with CVRD were reached (Rover, 1971a, Rover, 2005): evaluation of the equipment behavior; training of a new operation team (CVRD); evaluation of the product quality; and the investigation of the necessary parameters for the construction of the titanium production plant.

The original reactor was patented in a simpler and more efficient version, increasing production capacity, from 450 to 750 kg of sponge per operation, in the same time (72 hours) (Rover, 1971b).

Out of 30 operations as agreed with CVRD, 29 were effectively carried out, with consumption of around 64 tons of titanium tetrachloride, imported for the program. The pilot plant was operated in the condition of one operation a week, during 10 months of intensive training with the CTA team. At the end of the program, the CVRD team carried out the six last operations, without problems, having been judged ready to use the technology (Rover, 2005). The quality of the sponge produced in the AMR pilot plant was well within international norms. The Titanium Project ended in 1987. The titanium sponge blocks were broken up at the AMR (300t press) and the final milling was carried out at CVRD which commercialized part of the product. The Titanium Project evaluated normally with the total transfer of the technology developed in the CTA to a Brazilian company. This transfer was made with the complete participation of the CVRD technicians who were incorporated into the AMR teams and remained at the AMR premises for more than one year, observing and learning all the details of the titanium sponge production (Rover, 1970a, Rover, 1970b).

After more than one year of effective work, in a period of 20 years, the CTA transferred all the developed technology to CRVD, hoping that the patented process would be industrialized and it provided the necessary support for new research. In an additional gesture to facilitate the implantation of the titanium industry in Brazil, CTA transferred to CVRD all the equipment from its pilot plant. CVRD operated the pilot plant in Santa Luzia, Belo Horizonte, from June, 1988, having produced about 30t of titanium sponge. Financial difficulties and the reorientation of CVRD goals and objectives led its technology managers to suspend the plant operations in 1991. In 1994, CVRD returned the equipment that was brought back to AMR's warehouse (Henriques, 2008).

Process of titanium sponge production

The titanium sponge production in the AMR pilot plant was carried out using the Kroll process, which consists of $TiCl_4$ reduction by magnesium, in accordance with the following chemical reaction:

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

This operation was processed in a “reactor-retort”, so-called since the reduction and distillation operations were carried out in the same container as shown in Fig. 2 (Rover, 1970b).

A magnesium load (bars of 9 kg) should be heated to 750°C, for the titanium tetrachloride injection. The entire reaction is developed in an inert atmosphere (argon), due to the high titanium reactivity with atmospheric gases, preventing the final product contamination. In addition to titanium sponge, a large amount of $MgCl_2$ is formed as sub-product, that is poured out during the operation, leaving at the end, a sponge with Mg and $MgCl_2$ residual contents (Rover, 1971b).

The vacuum distillation stage is initiated with the action of the high vacuum system at 950C. Metallic magnesium and magnesium chloride vapors (used in excess in the reduction), are collected in the condenser. The operation lasts around 30 hours, depending on the amount of distilled material. The reactor is removed from the furnace, until it reaches room temperature. The cartridge is removed for cleaning, prior to a new reduction stage (Rover, 1971b).

Figure 2: Reactor-retort, equipment developed by CTA for titanium sponge production (Henriques, 2008).

The sponge is removed from the cartridge in a compact block of about 750 kg and stored for future breaking and melting as consumable electrode in vacuum. In industry's case, all the magnesium chloride obtained (from the reduction or distillation stages) would be recycled by means of electrolytic cells, returning to the system as chlorine and magnesium. The yield is around 70 per cent for chlorine and 90 per cent for magnesium. The chlorine would be sent in gaseous state to the chlorine plant and magnesium (liquid), taken directly to the reduction installation (Rover, 1973). Figure 3 shows the stages of the Kroll process used at CTA's plant [21].

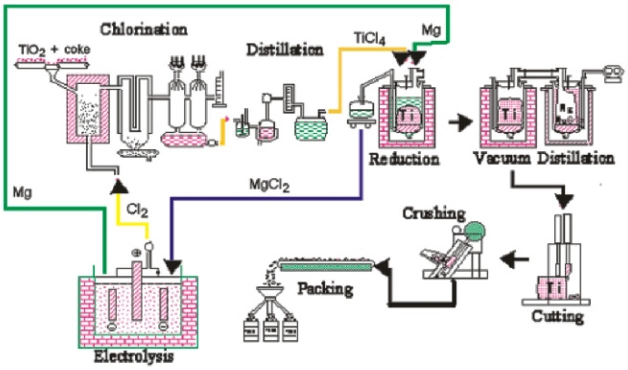


Figure 3: Stages of titanium sponge production (based on the Kroll process) used at the CTA plant (Henriques, 2008).

Titanium Ingot manufacturing

After the reduction and distillation stages, a final purification of the sponge is necessary using vacuum arc furnaces in order to eliminate residual impurities and to manufacture the ingots (Fig. 4).

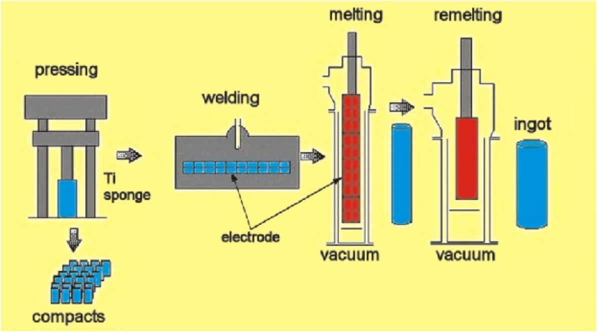


Figure 4: Titanium ingot manufacturing at CTA's plant (Henriques, 2008).

Manufacture of electrodes

The technique for manufacturing consumable electrodes from the titanium sponge includes compaction of sponge particles (15mm) and posterior welding of the compacts. A hydraulic press (100t) was used in the pressing stage, aimed at the production of ingots of 200mm in diameter (Faria, 1990). The pressing was carried out in a cylindrical die, with 52mm of internal diameter, without lubrication. The second stage consists of welding the compacts by means of resistance heating, in sufficient numbers to obtain the electrode. During the heating, the compacts are kept under stress. With this process, in addition to welding, an increase in the mechanical resistance of the compacts is obtained by sintering (Faria, 1990).

Melting and remelting of the consumable electrodes

The process commonly used in titanium ingot manufacture is vacuum arc melting with consumable electrode. This process uses the thermal energy of an arc as heat source. Due to the intense heat generated in the arc, a uniform "spray" flow is established from the melting electrode, that accumulates in the ingot-mold, forming a casting metal pool that solidifies rapidly (Henriques, 2008). The maintenance of a stable arc and a constant distance between the electrode and the casting metal is important for the metallurgic quality of the ingot (Faria, 1990). The flatter the pool, the less tendency for solute segregation or undesirable phase concentration. Factors affecting the mass transfer inside the pool due to thermal convection and interaction with the magnetic fields are also important. After the assembly of the electrode, start material (titanium chips) is deposited in the bottom of the ingot-mold, as a protective base. The chamber is closed and evacuated up to a pressure of $1,333x10^{-1}$ Pa. With the establishment of an arc between the electrode and the start material, the melting begins.

Direct polarity is used; the electrode is negative, where 2/3 of the power will concentrate in the metal pool (Henriques, 2008). Voltage gradients are relatively low, in the order of 20 to 50V, depending on some factors, including gas content in the furnace and the electrode, the required current, length of the arc, resistance of the electrode and ingot size (Henriques, 2008). Once the arc is initiated, the current is increased slowly to the desired level. This current will determine the melting rate, depth of the metal pool and surface quality of the ingot. Before the electrode melting is completed, the current is reduced gradually to allow the solidification of the metal pool to occur without the development of deleterious defects. After ingot cooling, the chamber is aired and a new electrode is fixed to the connecting rod and centered (Faria, 1990). On top of the first casting deposited in the ingot-mold, titanium chips must be placed, and, again, the chamber must be closed, vacuumed, repeating the entire procedure for the melting of the first electrode. The successive melting of about three electrodes is necessary to form a first melting ingot. The ingot, after final cooling, is removed from the ingot-mold and all the procedures are repeated for production of the next ingot, and so on repeatedly, until sufficient ingots are obtained to form an electrode for remelting.

The ends of the first melting ingots must be cut, top and bottom, and the surfaces must be smoothed for welding and remelting, after the ingot-mold removal. A remelting is considered necessary for all the applications to ensure an acceptable degree of homogeneity in the ingot (Faria, 1990). For a second remelting ingot production, it is necessary to weld the ingots face to face, to form an electrode of compatible size with the furnace dimensions and the desired final ingot. The welding of ingots is carried out in the melting furnace and after that, adequately centralized. The procedures for the melting of this new electrode are the same as for the ingots obtained from compacted sponge. Figure 5 presents a titanium sponge (750kg) and titanium ingot (260kg) produced at CTA during the 80s (Faria, 1990).

Powder metallurgy

With the completion of the Titanium Project at CTA, the Materials Division (AMR) began the development of powder metallurgy (P/M) techniques aimed at titanium alloy production, mainly because of the low production costs and the operation facilities.

Powder metallurgy is now a mature commercial metal-forming technology with the intrinsic advantage of net or near-net shape capability. P/M techniques afford designers the ability to produce significantly complex near-net shape parts at a potentially significant cost saving, with low material loss and it has been applied at CTA since 1998.

Unfortunately, the parts are limited in size and complexity, as well as being less than 100 per cent of theoretical density, which can adversely affect mechanical properties (Henriques, 1999, Henriques, 2001).

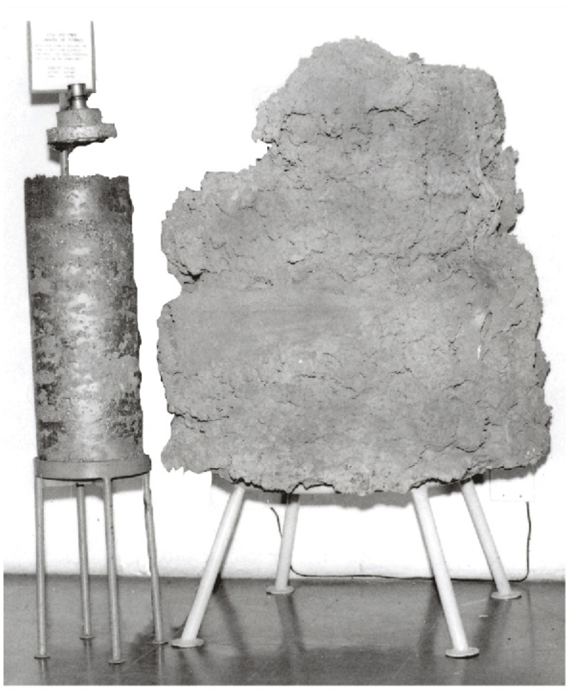


Figure 5: Titanium sponge (750kg) and titanium ingot (260kg) produced in CTA (Henriques, 2008).

Two methods are used to produce titanium powder from titanium ingots: hydride/dehydride and molten metal fragmentation. In the hydride/dehydride process, the ingot is exposed to hydrogen under conditions in which it forms a brittle titanium hydride. The brittle hydride is crushed to the required powder size, and then the conditions are altered to remove the hydrogen, thus producing titanium powder. In the molten metal fragmentation process, the titanium is melted and fragmented, either by centrifugal force on the rim of a spinning titanium disk, or by gas jet disruption of a molten titanium stream (Henriques, 2003a, Henriques 2003b). As with the process to produce titanium ingot, the processes required for titanium powder are also complex and inherently expensive. This forces the prices to be rather high and results in a very small market for titanium powder. A less expensive way is the use of titanium hydride powders (TiH) that can promote high final densification.

Titanium P/M preparation

At CTA, the process chosen for the preparation of the alloys includes the blended elemental method, using titanium hydrides followed by a sequence of uniaxial and cold isostatic pressings with subsequent densification by sintering. In this review, results of Ti-6Al-4V and Ti-13Nb-13Zr sintering are presented (Henriques, 2005, Henriques 2003c).

Titanium hydride powders are obtained by the HDH technique from Ti sponge fines. Hydriding is carried out at 500°C in a vertical furnace for 3 hours under a positive pressure. After cooling to room temperature, the friable hydride is milled in a niobium container under vacuum. Vanadium, niobium, tantalum, zirconium and other reactive metal powders for Ti alloy preparation are obtained using the same route, however with, significantly higher hydriding temperatures (800°C). Table 1 shows the principal characteristics of the powders used in Ti-6Al-4V samples.

Table 1: Characteristics of the powders used in the Ti-6Al-4V preparation (Henriques, 2005).

Characteristic	Ti	Al	V
Particle size (μm)	10	33	30
Morphology	Ang[a]	Sph[b]	Ang[a]
Melting point (°C)	1670	660	1890

[a] Ang Angular / [a] Sph Spherical

The starting powders are weighed and blended for 15 minutes in a double-cone mixer. After blending, the powders are cold uniaxially pressed at a pressure of 80 MPa, in cylindrical 20mm diameter dies. Afterwards, samples are encapsulated under vacuum in flexible rubber molds and cold isostatically pressed (CIP) at 350 MPa for 30 seconds in an isostatic press (Henriques, 2005).

Sintering and microstructural characterization

Sintering is carried out in a titanium or niobium crucible in high vacuum condition (10^{-7} Torr). Sintering temperatures ranged between 900 and 1500°C and heating rates of 20°C/min. After reaching the nominal temperature, samples are held at the chosen temperature for 1 to 2 hours and then furnace cooled to room temperature. Metallographic preparation is carried out using conventional techniques. Specimens are etched with a Kroll solution: (3mL HF: 6mL HNO_3: 100 mL H_2O) to reveal their microstructure. Microhardness measurements are carried out with load of 0.2 kgf. Photomicrographs are obtained using a scanning electronic microscope. The density of the sintered samples is determined by the Archimedes method (Henriques, 2003).

The influence of sintering temperature on the densification of the Ti-6Al-4V alloy was studied using isochronal sintering (holding time of 1h). Results are shown in Fig. 6. Density varies very little between 700 and 900C. Densification is speeded up between 900 and 1000C, the expected range for transus- with accompanying increase in diffusivity, reaching a maximum value of about 99.8 per cent of theoretical density at 1500C (Henriques, 2005).

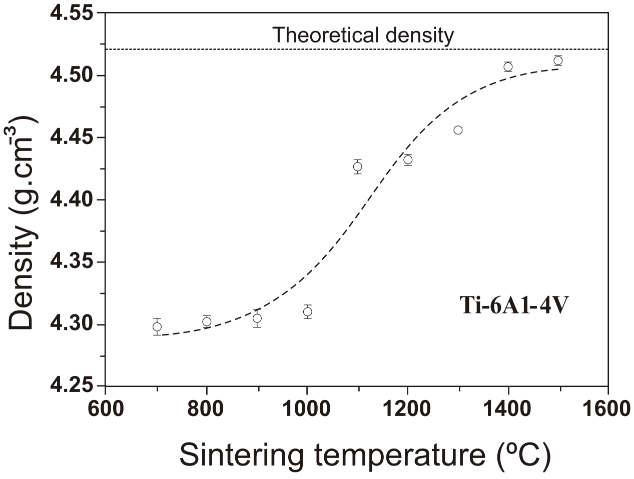


Figure 6: Plot of density vs. sintering temperature for Ti-6Al-4V. Dotted line indicates the theoretical density of the alloy (Henriques, 2005).

Microstructural development

Samples of Ti alloys present high densification, varying between 69 and 71 per cent of the theoretical specific mass after cold isostatic pressing, and between 93 and 95 per cent, after sintering, with homogeneous microstructure.

Most of the titanium alloys presented a Widmanstätten-like microstructure, two-phase (), with low porosity. The amount of the Widmanstätten microstructure increased with the sintering temperature. The hardness values are a function of the sintering temperature, lying in the range from 370 to 400 HV for the specimens prepared at 1500°C.

A typical issue related to the flow of hydrided powders is observed in the microstructural evolution. Hydrided powders present an angular and irregular morphology. With the enlargement of the surface area, the friction level in powder mass increases. Consequently, the friction between particles is high, providing low flow and packing rates. Figure 7 presents areas with agglomerations of niobium particles that occur due to the low powder flow, preventing a good homogenization between the elemental hydrided particles, which require high sintering temperatures to achieve the total dissolution of these agglomerates and complete homogenization of the alloy (Henriques, 2008).

An important fact in the microstructural development of titanium alloys produced by P/M is the dependence on the dissolution of metal particles with high melting points (normally β-stabilizers as Nb, V, Zr, Ta). Therefore, the microstructural development is only completed after the total dissolution of these elements in the titanium matrix which yields to a homogenous microstructure, as shown in Fig. 8 (Henriques, 2005).

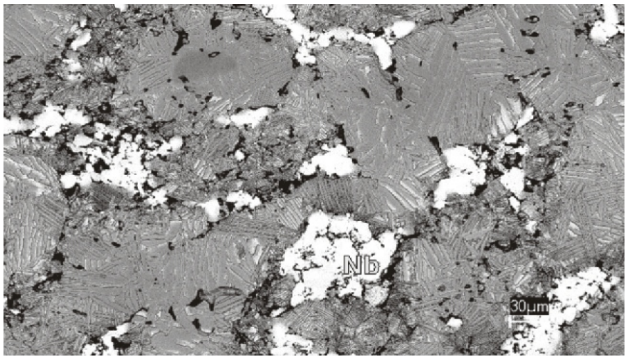
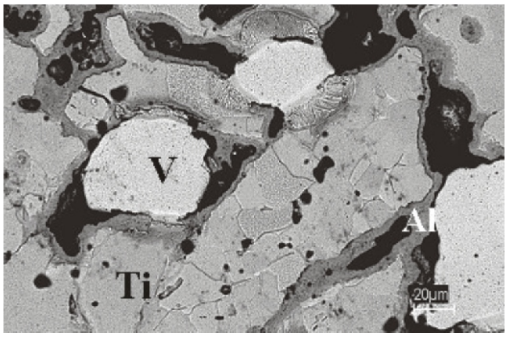
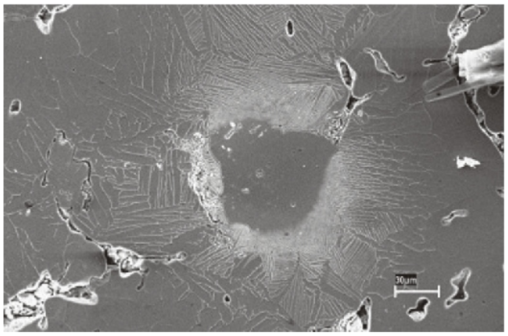


Figure 7: Microstructure of Ti-13Nb-13Zr sample sintered at 1100 °C presenting areas with niobium agglomerations (Henriques, 2008).

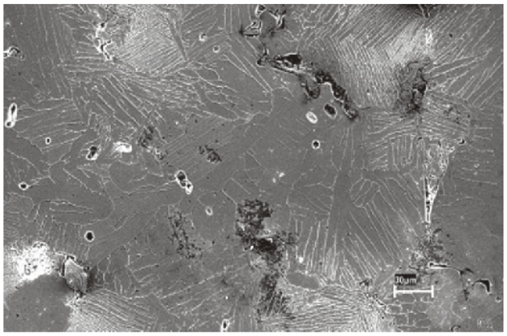
It can be observed that the Widmanstätten-like structure (basket weaved) grows with the dissolution of the -stabilizing particles through the increase in the sintering temperature. The dissolution of vanadium particles is very fast and at 1300C there are few regions without a two-phase microstructure. At the higher sintering temperature (/1500C), individual vanadium particles are found completely dissolved. Concerning the Widmanstätten microstructure, the dark-contrasting areas are -phase plates. The -phase, present among -plates, gives rise to a white contrast (Henriques, 2005).



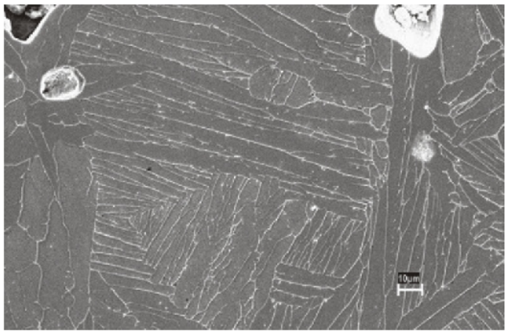
900 C



1100 C



1300 C



1500 C

Figure 8: Microstructural development of Ti-6Al-4V alloy showing the Widmanstätten growing from vanadium dissolution between 900 - 1500C (Henriques, 2005).

The expansion/contraction behavior during titanium alloy sintering brings important information in order to obtain high levels of densification. The sintering of Ti-13Nb-13Zr compacts using hydrided and dehydrided powders was investigated using a dilatometer (Henriques, 2008). The results are shown in Fig. 9.

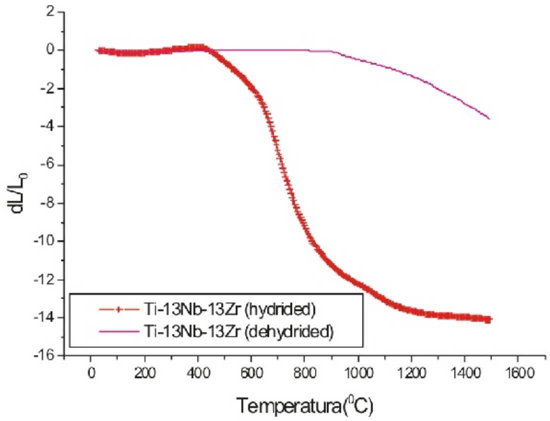


Figure 9: Expansion/contraction behavior in Ti-13Nb-13Zr sample sintered up to 1500C (Henriques, 2008).

In the Ti-13Nb-13Zr sample produced with dehydrided powders, the compacts expand slightly with the temperature increase. At 800C, contraction owing to densification starts. This temperature is close to the transus temperature of titanium powders.

Since the diffusivity of titanium is much higher than that of titanium, it is speculated that mutual diffusion between titanium and the other elemental powders is activated through the range of temperatures at which titanium is phase. Densification continued up to 1200°C and overall contraction exceeding 6 per cent was achieved. In the Ti-13Nb-13Zr sample produced with hydrided powders, after a slight expansion, the start of contraction is observed between 400-500ºC, close to the dehydriding temperature, which demonstrates the efficiency of the use of hydride powders in relation the dehydrided ones, mainly, in the velocity of the sintering mechanisms, that occur at lower temperatures, probably driven by the atomic movement caused by the diffusion of hydrogen and consequent generation of vacancies, that possess a basic importance in the mechanisms of mass transport and contraction during the sintering of parts produced by powder metallurgy (Henriques, 2001).

Densification continued up to 1200C and overall contraction exceeding 11 per cent was achieved (Henriques, 2008). This fact indicates the influence of hydrogen atoms in the sintering mechanisms providing a contraction even at low temperatures (Taddei, 2005, Taddei, 2004).

From these results, it was established that the route using blended elemental technique with hydrided powders is the most suitable for aerospace parts production, mainly because of the high densification reached.

CONCLUSIONS

Future titanium technology development efforts should be directed toward lower final components costs for the aircraft manufacturer. Increased emphasis on delivery cost will make it more difficult for titanium to maintain its share of the structural weight of aerospace systems unless the cost of the components can be reduced. There are two possible approaches, development of lower cost alloys and optimization of the processes in order to reduce the production costs.

More and more, engineers are coming to realize the benefits of titanium. This trend will continue and be enhanced through user education. Potential consumers need to be made aware of its outstanding properties, emerging lower cost processes, and its potential benefits to the life cycle of new applications.

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