TITANIUM PRODUCTION IN BRAZIL [1]

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Abstract

Titanium alloys parts are ideally suited for advanced aerospace system 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 research involving the metallic titanium in the Brazilian Aerospace Technical Center (CTA) occurred between 1965 and 1990, aiming to reduce the delay of the Brazilian research in relation to the developed countries. All developed technology was tranfered to the industry and the works provided the necessary technology of titanium sponge production, placing in the market more than14 tons, in a process just available to a closed group of industrialized countries. This work has for objective to rescue the importance of a historical period of the Brazilian metallurgy in the vacuum utilization for the reactive metals production. This work includes the evolution of the research with titanium in the CTA (powder metallurgy) and the current state-of-art of the titanium production in Brazil.

Key words: Titanium sponge; Titanium production; Vacuum; Powder metallurgy

PRODUÇÃO DE TITÂNIO METÁLICO NO BRASIL

Resumo

Titânio e suas ligas são muito utilizados no setor aeroespacial devido principalmente a sua elevada relação resistência mecânica/peso e excelente resistência à corrosão. As pesquisas envolvendo a obtenção de titânio metálico no Centro Técnico Aeroespacial (CTA) foram realizadas entre 1965 e 1990 e visavam reduzir a distância da pesquisa brasileira em relação aos paises desenvolvidos. Toda tecnologia desenvolvida foi repassada para a iniciativa privada. Os trabalhos realizados tornaram o Brasil auto-suficiente na tecnologia de produção de esponja de titânio, colocando no mercado brasileiro mais de 14 toneladas do produto, num processo só disponível a um fechado grupo de países industrializados. Este trabalho tem por objetivo resgatar a importância de um período histórico da metalurgia brasileira destacadamente na utilização, pioneira no país, da vacuometalurgia para o refino de metais e obtenção de ligas metálicas reativas e inclui a evolução dos trabalhos atuais envolvendo titânio no CTA (metalurgia do pó) e o atual estado-da-arte da obtenção do titânio e suas ligas no Brasil.

Palavras-chave: Esponja de titânio; Produção de titânio; Vácuo; Metalurgia do pó.

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1 INTRODUCTION

The studies of metallic titanium production in Brazil were initiated in the Military Institute of Engineering (IME), in 1965, as resulted of a final work of the metallurgic engineers, when were produced two small blocks of sponge with about 2 kg, each. In the same year, the Brazilian Air Force (MAer) carried out a first study aiming the development of titanium production techniques, not only for the use in aircrafts, but also aiming to create conditions in Brazil for: the consumption of the metal; the exploration of Brazilian ores and the development of a new technology in the treatment with reactive metals. These researches were pioneering in the use of vacuum equipment for melting and refining of metals in Brazil and were developed in the Materials Division (AMR) of the Aerospace Institute (IAE/CTA).

AMR initiated its works aiming to supply the necessities related at ferrous and non-ferrous materials, used in structural parts of aircraft and rockets.[1] The Group of metallurgical Processes (GPM) was created in 1965 for the development of reactive metallic alloys, in special titanium and zirconium. To reach such objectives, a laboratory with a complete infrastructure was mounted for the use of the following equipment of melting and refining: vacuum furnace -NRC, Vacuum Arc Remelting (VAR), Vacuum Induction Melting (VIM), Eletro-slag and a Electron Beam furnace - EB). This group of equipment was, to the time, the most expensive and productive pilot plant of a Research Center in Brazil. This group still generated an incalculable amount of reports, articles, books and theses. Since its formation the most important researchers of the Brazilian metallurgical area had taken part of its diverse teams of research. To cite some: Arno Müller (Titanium and vacuum metallurgy); Maurício Prates de Campos (Titanium and solidification); Iduvirges Lourdes Muller (Germanium); Carlos Firmo Schmidt Rover (Titanium); Murízio Ferrante (Titanium); e Paulo Remi Guimarães Santos (Titanium), among others. During this time the GPM developed lines of research in strategic materials as zirconium, uranium, magnesium, beryllium, germanium, refractory alloys and especially titanium. These works had an importance still not measurable in the advance of the national research in strategic materials. The GPM was pioneering in the use of the vacuum metallurgy for the metals refining and for the production of reactive metallic alloys, being the generator of the most important company of special alloys in Brazil, Eletrometal.[1]

1.1 Historical Importance of Titanium Project

The research carried out between 1965 and 1990 aimed to reduce the delay of the Brazilian research in relation to the developed countries, in the metallurgical area. All technology was developed aiming to be transferred for the private initiative and Brazil was close to possess an industry based in titanium and reactive metals. Titanium received a great investment on the part of the federal Brazilian government. For the CTA the Titanium Project was important for the following reasons: acquisition of wide experience in the titanium, that culminated with the concession of a patent, receiving of an important Brazilian Prize for innovation techniques in 1980 ; - it became Brazil self-sufficient in the titanium sponge production, in a process just available in a closed group of industrialized countries; still today the only successfully experience in the metallic titanium production in Latin America; - it served to place in the Brazilian market a reasonable amount of Ti sponge (only with the main program, it was produced in the CTA, from about 40 tons); - promote the knowledge of the technology of metallic chloride reduction and the production of reactive metals, such as zirconium, uranium, niobium and magnesium; and - the necessary experience in vacuum metallurgy for the manufacture of reactive alloys and metal refining, generating the advance of the Brazilian industry.[1]

1.2 Historical Facts about the Titanium Project

1965- The studies in the CTA start with the elaboration of the first project to the National Bank of Development (BNDE);
1966 - June - Construction of the pilot plant infrastructure; November - Signature of the contract with the BNDE;
1967 - Start of the assembly of the pilot-plant equipments;
1968 - Inauguration of pilot-plant - May – 1st operation of the $TiCl_4$ purification plant. Accident in the plant, with the titanium tetrachloride escape of 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 – 2nd operation of the reduction plant; July - operation of the reduction plant; August - 1st operation of the vacuum distillation plant; September – 2nd operation of the vacuum distillation plant.
1970 - 1972 - integrated operation of pilot-plant aiming to introduce modifications in the original equipments to: - the unification of the reduction and distillation plants; - operations in 100 kg of sponge scale;
1973 - 1976 - Operation in routine: - consolidation of the modifications. - production of 200 kg of sponge; - end of the main development works.
1977 - Request of patent to the INPI;
1977 - 1978 - Transference of the Titanium Project for the VALEP (subsidiary of Vale do Rio Doce, CVRD); 1979 - Interruption of the negotiations, due to the absence of customer; 1980 – Start of the negotiations with Metals of Minas Gerais METAMIG
1981 - October - Signature of the accord n.: 02-IPD/81, between CTA and METAMIG; 1982 - Execution of 1st program of work with the METAMIG;
1983 - 1985 - Interruption of the works due to financial problems with METAMIG; Negotiations with the CVRD for the transference of the accord n.: 02- IPD/81;
1986 - August - Signature of the Additive Term n.: 06-IPD/86, transferring accord CTA/METAMIG to the CVRD; September - Start of the work program with CVRD; 1987 - November - Ending of the work program with the CVRD. End of the titanium sponge production in the CTA.

1.3 Summary of the Titanium Project

In the accord with the CVRD the all goals were reached:[2] evaluation of the equipment behavior; training of a new operation team (CVRD); evaluation of the product quality; - Survey of the necessary parameters to the first production plant of titanium sponge. The original reactor was patented in a simpler and efficient version. Increasing the production capacity of the reactors – from 450 up to 750 kg of sponge for run, in the same time (72 hours).

From 30 runs of accorded 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 run a week, during 10 months of intensive training with the CTA team. In the end of the program the CVRD team carried out the 6 last runs, without problems, having been considered apt to use the technology. The quality of the sponge produced in the AMR pilot plant is near the international norms. The Project Titanium finished in 1987, November. The blocks of titanium sponge were broken in the AMR (300 ton press) and the final milling, was made in the CVRD that commercialized part of the product. The Titanium Project evaluated normally with the total transference of the technology developed in the CTA for a Brazilian company. Such transference was made in the most complete participation of the CVRD technicians who were incorporated at the AMR teams and remained in the Division dependences for more than one year, observing and learning all the details of the titanium sponge production.

After more than one year of effective work, in a period of 20 years, the CTA transferred all the developed technology to the CRVD, hopping that the patented process was industrialized and provided the necessary subsides to the new research. As additional form to facilitate the implantation of the titanium industry in Brazil; the CTA transferred to the CVRD all the equipments of its pilot plant. The CVRD operated the pilot plant in Santa Luzia, Belo Horizonte, from june, 1988, having produced about 30 tons of titanium sponge. Financial difficulties and reorientation of goals and objectives of the CVRD had taken its Supervision of Technology to suspend the operations of the plant in 1991. In 1994 the CVRD returned the equipments that were collected to the AMR deposits.

1.4 Process of Titanium Sponge Production

The titanium sponge production, in the AMR pilot plant, was carried out by the Kroll Process, which consists in the $TiCl_4$ reduction by magnesium, in accordance with the following chemical reaction: $TiCl_4 + 2Mg \rightarrow Ti + 2MgCl_2$. This operation is processed in a "reactor-retort", thus called since the reduction and distillation operations are carried out in the same container. A magnesium load (bars of 9kg) was heated until 750 °C, for the titanium tetrachloride injection. All the reaction is developed under inert atmosphere (argon), in virtue of the high titanium reactivity with the atmospheric gases that can contaminate the final product. Beyond the titanium sponge, is formed as sub-product, a high amount of $MgCl_2$ that is poured during the operation, remaining in the end, the sponge contend Mg and residual $MgCl_2$. The vacuum distillation is initiated with the action of the high vacuum systems of and furnace heating at 950 °C. The metallic magnesium and magnesium chloride vapors (used in excess in the reduction), were collected in the condenser. The operation lasted about 30 hours, depending on the amount of distilled material. The reactor was removed of the furnace during 24 h, until it reaches the room temperature. The cartridge was removed for cleanning, for a new reduction. The sponge was removed of the cartridge in a compact block with about 750 kg and stored for future breaking and melting for consumable electrode in vacuum. In the case of an industry, all the magnesium chloride obtained (of the reduction or the distillation in vacuum) would be recycled by means of electrolytic cells, coming back to the system as chlorine and magnesium. The exploitation is around 70% for chlorine and 90% for magnesium. The chlorine would be sent in gaseous state for the installation of chlorine and magnesium, liquid, taken directly for the reduction installation. Figure 1 indicates the evolution in the reduction process plant.

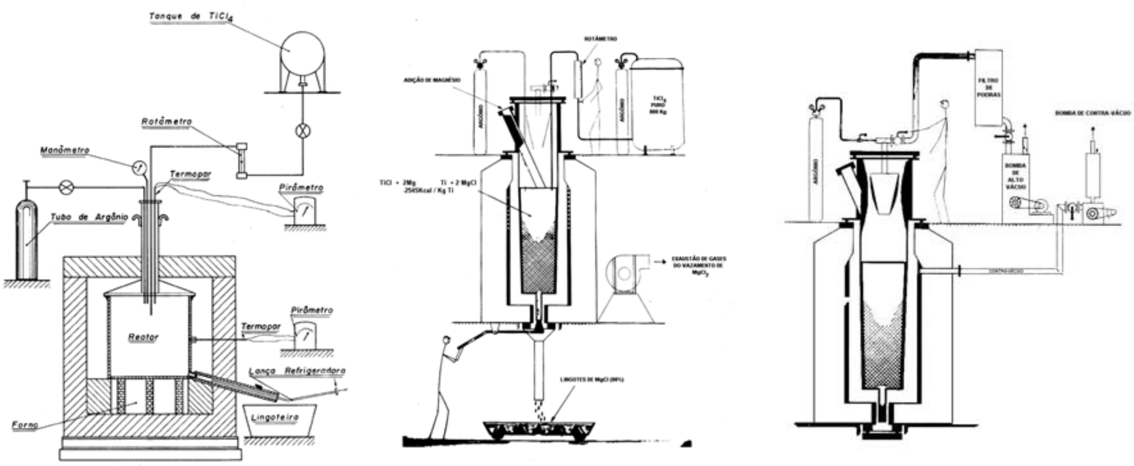


Figure 1- Evolution in the reduction process plant.[3]

1.5 Manufacture of Consumable Electrodes

The technique of manufacture of electrodes from the titanium sponge consists of the sponge pressing and posterior welding of the compacts. a hydraulic press (100 tons) is used in the pressing stage, aiming the production of ingots with 200 mm of diameter. The pressing is carried out in a cylindrical, composed matrix, with 52 mm of internal diameter, without lubrication. The second stage consists of the welding of the compacts by means of a resistance heating, in a number enough to obtain the electrode. During the heating, the compacts are kept under stress. With this process, beyond the welding, an increase of the resistance mechanics of the compacts is obtained by sintering.[4]

1.6. Melting and Remelting of the Consumable Electrodes

The process more commonly used in the titanium ingot manufacture is the vacuum arc melting with consumable electrode. This process uses the thermal energy of an arc as heat source. In virtue of the intense heat generated in the arc, a "spray" with an uniform flow is established from the electrode melting, that accumulates in the ingot-mold, forming a casting metal pool that is rapidly solidified.[4] 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.[5] The more flat is the pool, minor the trend of solute segregation or undesirable phases concentration. Factors with influence on the mass transference inside the pool due to thermal convection and interaction with the magnetic fields are also important.[5] After the assembly of the electrode, start material (titanium chips) is deposited in the bottom of the ingot-mold, on a protection base. The chamber is closed and evacuated until a pressure of $1,333x10^{-1}$ Pa. At the establishing of an arc between the electrode and the start material the melting is started. The direct polarity is used, the electrode is negative, and in way that 2/3 of the power will concentrate in the metal pool.[6] The voltage gradients are relatively low, in the order from 20 up to 50V, depending on some factors, including the gas content in the furnace and the electrode, required current, length of the arc, resistance of the electrode and ingot size.[4,5] After initiate the arc, the current is increased slowly for the desired level. This current will determine the melting rate, depth of the metal pool and superficial quality of the ingot. Before the complete electrode melting, the current is reduced gradually to allow that the solidification of the metal pool occur without the development of deleterious defects. After the cooling of the ingot, the chamber is aired and a new electrode is fixed to the connecting rod and centered.[7] Over the first casting deposited in the ingot-mold, titanium chips must be placed, and, again, the chamber must be closed, vacuumed, repeating all the procedure for the melting of the first electrode. The successive melting from about three electrodes is necessary to form a first melting ingot. The ingot, after enough cooling, is removed of the ingot-mold and all the procedures are repeated for production of the next ingot, and thus successively, until the obtainment of an ingot number enough to form an electrode for remelting.

The ingots of the first melting must suffer the cut from the extremities, head and foot, and the surfaces must be smoothed for welding and remelting, after the ingot-mold removal. A remelting is considered necessary for all the applications for assuring an acceptable degree of homogeneity in the ingot. For the obtainment of a second remelting ingot becomes 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 of the ingots obtained from compacted sponge.[7]

1.7 Powder Metallurgy

With the finish of the Titanium Project in CTA, the Materials Division (AMR) began the development of powder metallurgy (P/M) techniques aiming the titanium alloys production, mainly because its low production costs. P/M 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 savings, with low material loss and is being applied in CTA since 1998. Unfortunately, parts are limited in size and complexity, as well as less than 100% of theoretical density, which would adversely affect mechanical properties.[8,9]

In the present work, the microstructural evolution in Ti-6Al-4V alloy has been investigated in detail.

2 MATERIALS AND METHODS

The blended elemental method followed by a sequence of uniaxial and cold isostatic pressing with subsequent densification by sintering was chosen for the preparation of the alloys.

Titanium powders were obtained by the HDH technique from chips. Hydriding was carried out at 500° C in a vertical furnace for 3 hours under a positive pressure. After cooling to room temperature, the friable hydride was milled in a niobium container under vacuum. The dehydriding stage was carried out at 500 °C in dynamic vacuum conditions. Vanadium powder was obtained using the same route, however, hydriding-dehydriding temperatures were significantly higher (800° C). Valimet supplied aluminum powder. Table 1 shows the principal characteristics of those powders.

Table 1 - Characteristics of the powders used in the Ti-6Al-4V preparation.

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

[a] *Ang – Angular*
[b] *Sph – Spherical*

The starting powders were weighed (10 grams) and blended for 15 minutes in a double-cone mixer. After blending, the powders were cold uniaxially pressed under a pressure of 80 MPa, in cylindrical 20 mm dia.-dies. Afterwards, samples were encapsulated under vacuum in flexible rubber molds and cold isostatically pressed (CIP) at 350 MPa during 30 s in an isostatic press.

Sintering was carried out in titanium crucible in high vacuum condition (10^{-7} Torr), using a Thermal Technology Inc. Astro 1000 equipment. Sintering temperatures ranged between 900 and 1500° C and heating rates of 20°C/min. After reaching the nominal temperature, samples were hold at the chosen temperature for 1 h and then furnace cooled to room temperature. Metallographic preparation was carried out using conventional techniques. Specimens were etched with a Kroll solution: (3mL HF: 6mL HNO_3: 100 mL H_2O) to reveal its microstructure. Microhardness measurements were carried out in a Micromet 2004 equipment, Buehler, with load of 0.2 kgf. The photomicrographs were obtained using a SEM LEO model 435VPi. The density of the sintered samples was determined by the Archimedes method.

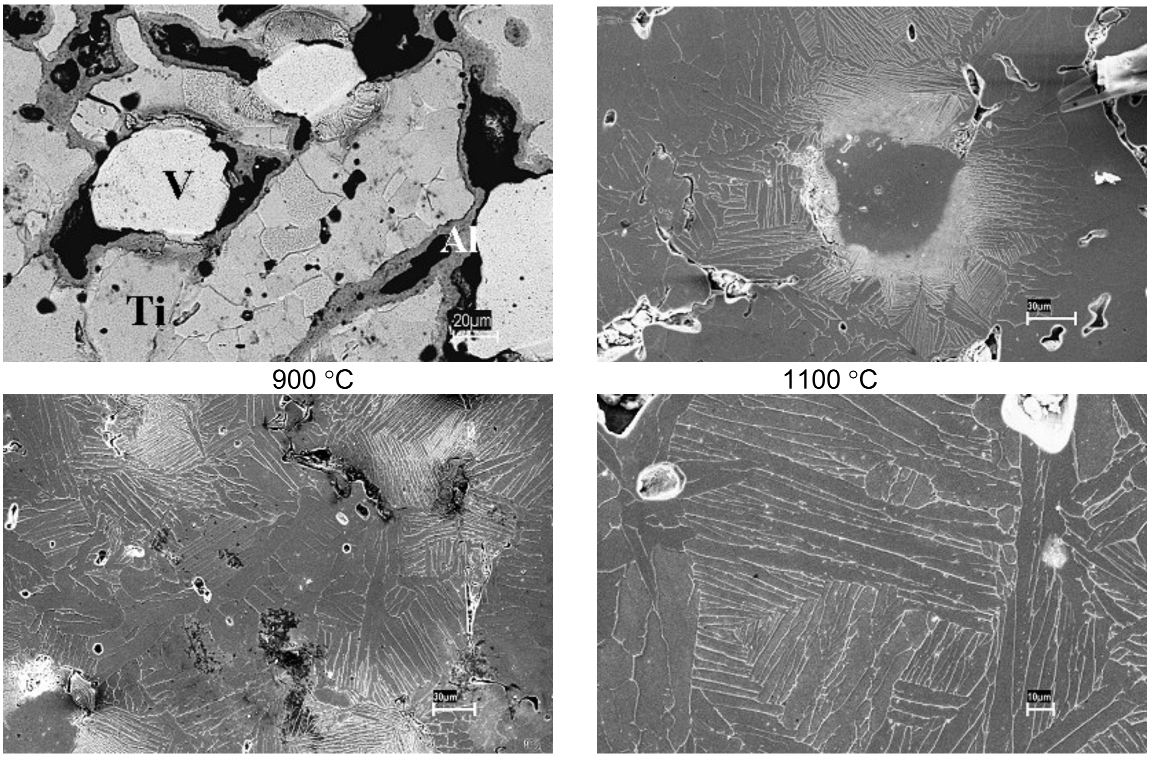
3 RESULTS AND DISCUSSION

The samples presented high densification, varying between 69 and 71% of the theoretical specific mass, after cold isostatic pressing and, among 93 and 95%, after sintering, with homogeneous microstructure.

The Ti-6Al-4V samples after sintering (Figure 2), presented a Widmanstätten-like microstructure, two-phase ($\alpha+\beta$), with low porosity. The amount of the Widmanstätten-like microstructure increased with the sintering temperature. The hardness values were function of the sintering temperature, lying in the range from 370 to 400 HV for the specimens prepared at 1500°C. At lower sintering temperatures, the obtained microstructure is inhomogeneous and display coarse porosity. The hardness commonly reported for hot wrought alloys is about 350 HV.[10]

The Ti-6Al-4V samples sintered at 1500°C, presented the best results when compared to the microstructure found in commercial samples. It can be observed, a Widmanstätten-like microstructure distributed throughout the sample (Figure 1). Concerning the Widmanstätten microstructure, the dark-contrasting areas are α-phase plates. The β-phase, present among α-plates, gives rise to a white contrast.

In the Ti-6Al-4V, at 1000°C, begins the formation of the two-phase Widmanstätten structure starting from the vanadium particles, that act as β-phase nucleation agent. It can be observed that the Widmanstätten structure grows with the dissolution of the β-stabilizator particles by increase of the sintering temperature.



900 °C 1100 °C

1300 °C 1500 °C

Figure 2- Microstructural development of P/M-Ti-6Al-4V alloy showing the Widmanstätten growing from vanadium dissolution between 1000-1500 °C.

4 CONCLUSIONS

1- The Titanium Project became Brazil self-sufficient in the titanium sponge technology, in a process only available in a closed group of industrialized countries. Still today it is the unique experience successfully of a Latin America country in the metallic titanium production.
2- The Titanium Project propitiated the knowledge of the reactive metal technology and metallic chloride reduction, from materials as zirconium, uranium, niobium and magnesium.
3- The Titanium Project propitiated the necessary experience in vacuum metallurgy for the manufacture of reactive alloys and metal refining for the technological development promoting the advance of the Brazilian industry.
4- The quality of the sponge produced in the pilot plant is the same of the international norms.
5- The blended elemental process demonstrated to be efficient for the Ti-6Al-4V alloy production by powder metallurgy. The samples presented a good densification and adequate microstructure.
6- Combination of relatively low-cost powders, compaction techniques with high productivity, minimal machining and good mechanical properties can provide titanium parts produced by P/M more attractive in aerospace applications.

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