Titanium Powder Metallurgy:

A Review - Part 1

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Titanium and its alloys are the materials of choice for many applications, but high cost often negates their use. Powder metallurgy offers a cost-effective fabrication approach.

Titanium alloys are among the most important advanced materials that are key to improved performance in aerospace and terrestrial systems [1-5]due to their excellent combinations of specific mechanical properties (properties normalized by density) and outstanding corrosion behaviors [6-10] . However, limiting widespread use of Ti alloys is their high cost compared to competing materials. This has led to numerous investigations of various potentially lower-cost processes [1-3] including powder metallurgy (PM) techniques [1-2,6-10,12,13] This article discusses titanium PM technology including the blended elemental (BE) approach, prealloyed (PA) methods, additive layer manufacturing (ALM), metal injection molding (MIM), and spray deposition (SD) processing. Not discussed are far-from-equilibrium processing (rapid solidification, mechanical alloying, and vapor deposition) and porous materials and powders for attaching to the surface of body implants. A more comprehensive review of titanium PM will be published in 2013 [4] .

The cost of fabricating various titanium precursors and mill products has been discussed in several publications over the past few years [1-3] ,noting that the cost of extraction is a small fraction of the total cost of a component fabricated via the cast and wrought (ingot metallurgy) approach (Fig. 1). To produce a final component, the mill products shown in Fig. 1 must be machined, often with very high buy-to-fly ratios (which can reach as high as 40:1). The generally accepted cost of machining a component is

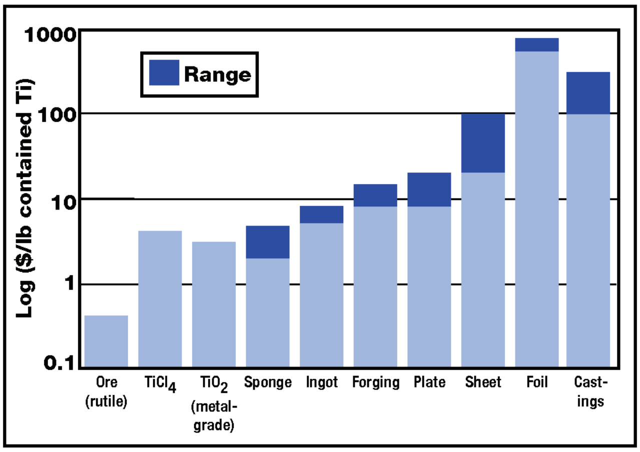

Fig. 1 - Cost of titanium at various stages of component fabrication.

TABLE 1 — CHARACTERISTICS OF DIFFERENT TYPES OF TITANIUM POWDERS(a)

Type/process	Powder type	Advantages	Status/disadvantages
Hunter process (pure sodium)	Elemental	Low cost; excellent for cold press and sinter	Limited availability; high chloride
HDH(b) Kroll process (pure magnesium)	Elemental	Lower cost; good compactability; readily available; low chloride	
HDH powder produced from alloys	Prealloyed	Readily available	High cost; fair compactability
Atomized	Prealloyed	High purity; available	High cost; not cold compactable
REP/PREP(c)	Prealloyed	High purity	High cost; not cold compactable
ITP (International Titanium Powder)/Armstrong	Elemental & Prealloyed	Compactable; moderate cost; potential for low cost	Processibility/quality; production scale-up
Fray	Elemental & Prealloyed	TBD	Developmental
MER(d)	Elemental & Prealloyed	TBD	Developmental
CSIRO TiRO(e)	Elemental & Prealloyed	TBD	Developmental

(a) Modified from Abkowitz, et al.[15]. (b) Hydride-dehydride. (c) Rotating electrode powder/plasma rotating electrode powder. (d) MER Corp., Tucson, Ariz. (e) CSIRO, Melbourne, Australia.

that it doubles the cost of the component (with the buy-to-fly ratio being another multiplier in cost per pound) as shown in Fig. 2. This means that anything that can be done to produce a component closer to the final configuration will result in a cost reduction-hence the attraction of near-net-shape PM components.

Titanium powder metallurgy

Table 1 shows the characteristics of the different types of titanium powders that are either available or under development today. The table is based in part on a recent review of powder-production methods coauthored by McCracken [14] . The oxygen level of the hydride-dehydride (HDH) powder can be reduced by deoxidizing with calcium[14] . It is also possible to convert the angular HDH to a spherical morphology using the Telma process discussed later.

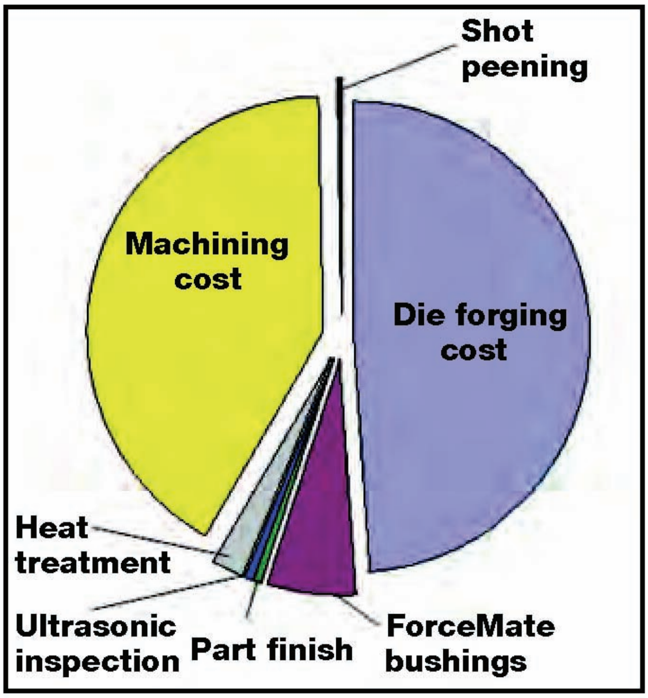

Fig. 2 - Boeing 787 side-of-body chord manufacturing cost breakdown. Courtesy of Boeing.

Development of new titanium production methods such as the ITP / Armstrong, Fray, CSIRO (Commonwealth Scientific and Industrial Research Organization, Australia), and MER processes shown in Table 1 is aimed at lowering the cost of PM titanium powder. However, these powders are not yet available, and their relative cost and processing characteristics are yet to be established.

Companies/processes that produce prealloyed spherical titanium powder include:

- ATI Powder Metals, Pittsburgh, Pa. (formerly Crucible Research Center); spherical gas-atomized alloy powder; 100-lb capacity melting furnace.
- Advanced Specialty Metals, Nashua, N.H.; spherical plasma rotating electrode process (PREP).
- Raymor Industries Inc., Boisbriand, Quebec, Canada (now includes Pyro genesis); spherical plasma atomized.
- Baoji Orchid Titanium Industry Co. Ltd., China; spherical PREP.
- ALD Vacuum Technologies, Hanau, Germany; electrode induction melting gas atomized spherical Ti-6Al-4V powder.
- Sumitomo Sitex, Japan; gas atomized Ti-6Al-4V powder (0.08-0.13 wt% oxygen).
- TLS Technik GmbH & Co., Bitterfeld, Germany; gas atomized.
- Affinity International; gas atomized and PREP (may be out of business).

-Towa State University/ Ames Lab; experimental gas atomization; cost effective; very fine spherical powder (<325 mesh, or 45 μm) produced using a close-coupled high pressure supersonic gas. Plans are to commercialize the process under a company called Iowa Powder Atomization Technologies.

- Tekna Induction, Sherbrooke, Quebec, Canada; plasma spheriodization process converts irregular shaped titanium powder (-100/+400 mesh, or -150/+37 μm) to a spherical morphology of the same size range, but with a significant improvement in tap density and flow rate.
- Quad Cities Manufacturing Laboratory, Rock Island, Ill.; plans to establish capabilities for PREP, gas atomization, HDH, and the Telma induction plasma spheriodization process (to convert HDH powders).

Atomized powders are generally prealloyed and spherical (Fig. 3a). Sponge fines (a byproduct of sponge production) are angular, sponge-like in nature, and contain remnant salt, which prevents achievement of full density and adversely affects weldability (Fig. 3b). Hydride-dehydride powders, which are generally also prealloyed, are angular in nature (Fig. 3c)[16] . Conversion to a spherical morphology using the Telma process is shown in Fig. 3d.

Nonmelt processes

Four non-melt processes appear to have the greatest potential for scale-up, with an additional process being developed by Advance Materials (ADMA) Products, Hudson, Ohio, which is also of potential commercial interest. The processes are the FFC Cambridge approach, the MER technique, the (CSIRO) methods, and the ITP/Armstrong process. In the FFC Cambridge approach, titanium metal is produced at the cathode in an electrolyte (generally $CaCl_2$) by the removal of oxygen from the cathode. This technique allows the direct production of alloys such as Ti-6Al-4V at a cost that could be less than product of the conventional Kroll process[17] . The process is being developed by Metalysis in South Yorkshire, UK.

The MER approach is an electrolytic method that uses a composite anode of TiO_2, a reducing agent, and an electrolyte, mixed with fused halides. Projections are for titanium production at a significantly lower cost than the conventional Kroll process [18] .

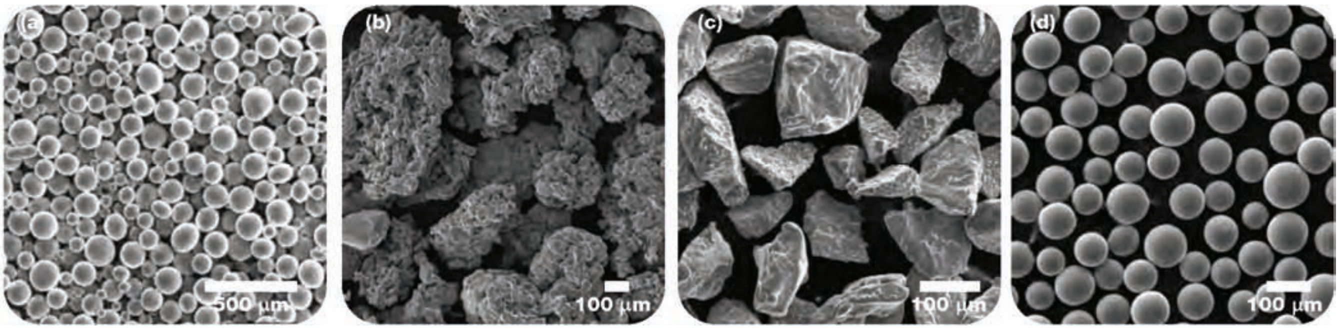

Fig. 3 - (a) SEM photomicrograph of gas-atomized prealloyed spherical Ti-6Al-4V (courtesy of Affinity International); (b) SEM photomicrograph of sponge fines produced by the Kroll process (courtesy of Ametek); (c) SEM photomicrograph of angular HOH titanium powder; and (d) SEM photomicrograph of spherical powder produced by processing angular HOH titanium to a spherical morphology using the Tekna technique.

The CSIRO technique [19] builds upon the fact that Australia has some of the largest mineral and sand deposits in the world. In this approach, cost-effective commercially pure titanium is produced in a continuous fluidized bed in which titanium tetrachloride is reacted with molten magnesium (the TiRO process). They also have a proprietary process for producing alloys (details unavailable at the present time). Continuous production of a wide range of alloys including aluminides and Ti-6Al-4V has been demonstrated on a large laboratory scale. The commercially pure titanium powder produced was used to fabricate extrusions, thin sheet by continuous roll consolidation, and cold-spray complex shapes including ball valves and seamless tubing. Commercialization of the process is now in the planning stage with a decision to proceed to the pilot plant stage likely to be taken in 2012.

The ITP/ Armstrong method [1-3] is continuous and uses molten sodium to reduce titanium tetrachloride, which is injected as a vapor. The resultant powder does not need further purification and can be used directly in the conventional ingot approach. The powder is most efficiently used in the powder metallurgy technique. A range of alloys can be produced (including the Ti-6Al-4V alloy) as a high quality homogeneous product suitable for many applications. ITP currently operates an R&D facility in Lockport, Ill., and has broken ground on a four million pound per year expansion in Ottawa, Ill., which is expected to ramp up production throughout 2012, and will produce both commercially pure titanium and Ti-6Al-4V alloy powder.

Fig. 4 - Auto connecting rod fabricated via blended elemental approach using hydrogenated titanium powder.
Courtesy of Orest Ivasishin, Ukrainian Academy of Sciences

Fig. 5 - The Toyota Altezza (1998 Japanese car of the year) is the first family automobile in the world to feature titanium valves; Ti-6Al-4V intake valve (left) and TiB/Ti-Al-Zr-Sn-Nb-Mo-Si exhaust valve (right). Courtesy of Toyota Central R&O Labs Inc.

In the ADMA Products approach [20] , sponge titanium is cooled in a hydrogen atmosphere rather than the conventional inert gas. The hydrogenated sponge is then easily crushed, and in the hydrogenated condition can be compacted to a higher density than conventional low-hydrogen sponge; subsequent hydrogen removal is easily accomplished with a simple vacuum anneal. The remnant chloride content of the hydrogenated sponge is reported to be at low levels (helping to avoid porosity and enhancing weldability). There are 14 patents covering this approach.

Estimates of the powder shipments (annually in all cases) are HDH (1000-2500 metric tons worldwide and 200-400 metric tons U.S.) and spherical (150-350 metric tons worldwide and 20-50 metric tons U.S.).

Near-net shapes

Techniques generally available for production of near net shapes (NNS) are amenable for use with various types of titanium powders; these include conventional press-and-sinter, elastomeric bag cold isostatic pressing (CIP), and ceramic mold or metal can hot isostatic pressing (HIP). Production of NNS is divided into parts produced using blended elemental powders and those produced using prealloyed powders.

The blended elemental approach is potentially the lowest cost titanium PM process, especially if any secondary compaction step (e.g., HIP) can be avoided [15,21] . In the process, angular titanium sponge fines (or titanium hydride powder) and master alloy composition (generally the 60 Al:40 V variety to produce the Ti-6Al-4V composition) are blended together, cold pressed, and sintered to near full density. Use of titanium hydride enables achieving densities very close to 100% in components such as the auto connecting rod shown in Fig. 4, with mechanical properties at ingot-metallurgy levels.

Blended-element PM technology using hydride-dehydride (HDH) titanium powder produced by the Kroll sponge process is the key to the commercial success of Dynamet Technology Inc'.s (Burlington, Mass.) PM process [15] , which is producing a wide range of affordable PM mill products. Figure 5 shows valves made using the BE process for production models of the Toyota Altezza family automobile [1-3] .

TABLE 2 — TENSILE PROPERTIES FOR TI-6AL-4V ALLOY

Material	% theoretical density	Ultimate tensile strength, MPa (ksi)	Yield strength, MPa (ksi)	Elongation, %
AMS 4928 (min)		896 (130)	827 (120)	10
Typical wrought		965 (140)	896 (130)	14
Typical PM CIP-sinter	98	951 (138)	841 (122)	15
Typical PM CHIP	100	965 (140)	854 (124)	16

TABLE 3 — MECHANICAL PROPERTIES OF FORGED ANNEALED TI-6AL-4V PM COMPACTS(a)

Material	Ultimate tensile strength, MPa (ksi)	Yield strength, MPa (ksi)	Elongation, %	Reduction of area, %
3.5 cm (1.376 in.) thick	994-1028 (144-149)	911-938 (132-136)	14.0-15.5	34-38
ASTM Specification	897 (130)	828 (120)	10	25

(a) Produced from cold pressed and sintered hydrogenated titanium powder.

Currently, ADMA Products' hydrogenated titanium powder manufacturing capacities are 50,000-60,000 lb/yr, and the company is installing a pilot scale unit that will triple output [22] . Results of tests conducted by major aircraft companies and the U.S. DOE and DOD show that properties of the PM Ti alloys meet AMS specification and meet or exceed properties of titanium wrought alloys made using conventional ingot-metallurgy approaches.

CHIP process

Dynamet Technology uses the CIP-sinter or CHIP (CIP-sinter-HIP) process to produce NNS parts for finish machining to high tolerance configurations and performs [15] . The sintering process was historically established to reach a minimum density level at which the material had no interconnected porosity. At this density threshold, the material could be hot isostatically pressed without the processing expense of HIP encapsulation, making it economically viable. Recent developments enabled achieving greater than 98% sintered density, resulting in as-sintered tensile properties equivalent to those of wrought material and superior to those of castings as shown in Table 2 [15] .

This reduces the need for HIP and further strengthens the economic advantage of PM CIP-sinter manufacturing technology.

Hydrogenated titanium process

The use of titanium hydride powder instead of titanium sponge fines led to the achievement of essentially 100% density in complex parts using a simple, cost-effective press-and-sinter technique [20,21] . ADMA Products produced a lower cost titanium hydride powder by cooling sponge produced in a Kroll process with hydrogen rather than the conventional inert gas. The hydrogenated non Kroll powder was used together with 60 Al:40 V master alloy to produce components made of the Ti-6Al-4V alloy. Typical mechanical properties after cold pressing, sintering, forging, and annealing are shown in Table 3. The mechanical properties compare well with those exhibited by cast and wrought products. The low cost of the process in combination with the attractive mechanical properties make the approach well suited to the cost-obsessed automobile industry. A General Motors connection link weighing about 0.705 lb (0.32 kg) was estimated to be less than $3.00 [23] .

In the Kroll process, removal of Ti sponge from the retort and its subsequent crushing is time and energy intensive. In comparison, ADMA's process produces TiH_2 that, unlike Ti sponge, is very friable and easily removed from retort with no need for an expensive sizing operation. ADMA's vacuum distillation processing time is also at least 80% less than in the Kroll process, because phase transformations/lattice parameter changes of the hydride sponge in the presence of hydrogen accelerate distillation removal of $MgCl_2$. Finally, atomic hydrogen is released during sintering-dehydriding of TiH_2 powder, and serves as a scavenger for impurities (e.g., oxygen, chlorine, magnesium, etc.) resulting in titanium alloys with low interstitials that at least meet properties of ingot-metallurgy alloys, both static and S-N fatigue behavior [12] .

Powders can be subsequently fabricated to other product forms such as sheet. Alloy sheet can be fabricated in a similar manner by adjusting the feed stock to a mixture of titanium powder and alloying additions.

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